

FINAL REPORT
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MONITORING OF ATMOSPHERIC PARTICLES AND OZONE
IN SEQUOIA NATIONAL PARK: 1985-1987

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ABSTRACT

The report describes a three-year project (1985-87) conducted by the Air Quality Group of Crocker Nuclear Laboratory to monitor atmospheric particles and ozone in Sequoia National Park, as part of an attempt to understand the impact of acid deposition and other air pollutants on the park's ecosystem.

The project undertook extensive measurements of particulate matter which were then correlated with meteorology, known elemental sources, and wet and dry deposition. For high-altitude ozone measurement, the project developed a new solar-powered ozone monitoring system.

After background discussion of the air pollution meteorology of Sequoia and the surrounding area, the report discusses first atmospheric particle monitoring and then ozone monitoring, along with the results of each.

The results show that particulate matter at Sequoia is similar to that present at other sites on the western slope of the Sierra Nevada range at equivalent elevations, although some anthropogenic species including nickel and sulfate are higher at Sequoia than at Yosemite National Park. The source of most of the particles is the San Joaquin Valley, with efficient transport by terrain-effect winds to elevations above 6000 feet. By 10,000 feet, however, this transport is greatly weakened. The ozone profiles show a similar behavior with elevation. Daytime ozone levels at 6000 feet are equivalent to those on the valley floor, but decrease abruptly by 10,000 feet.

DISCLAIMER

The statements and conclusions in this report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

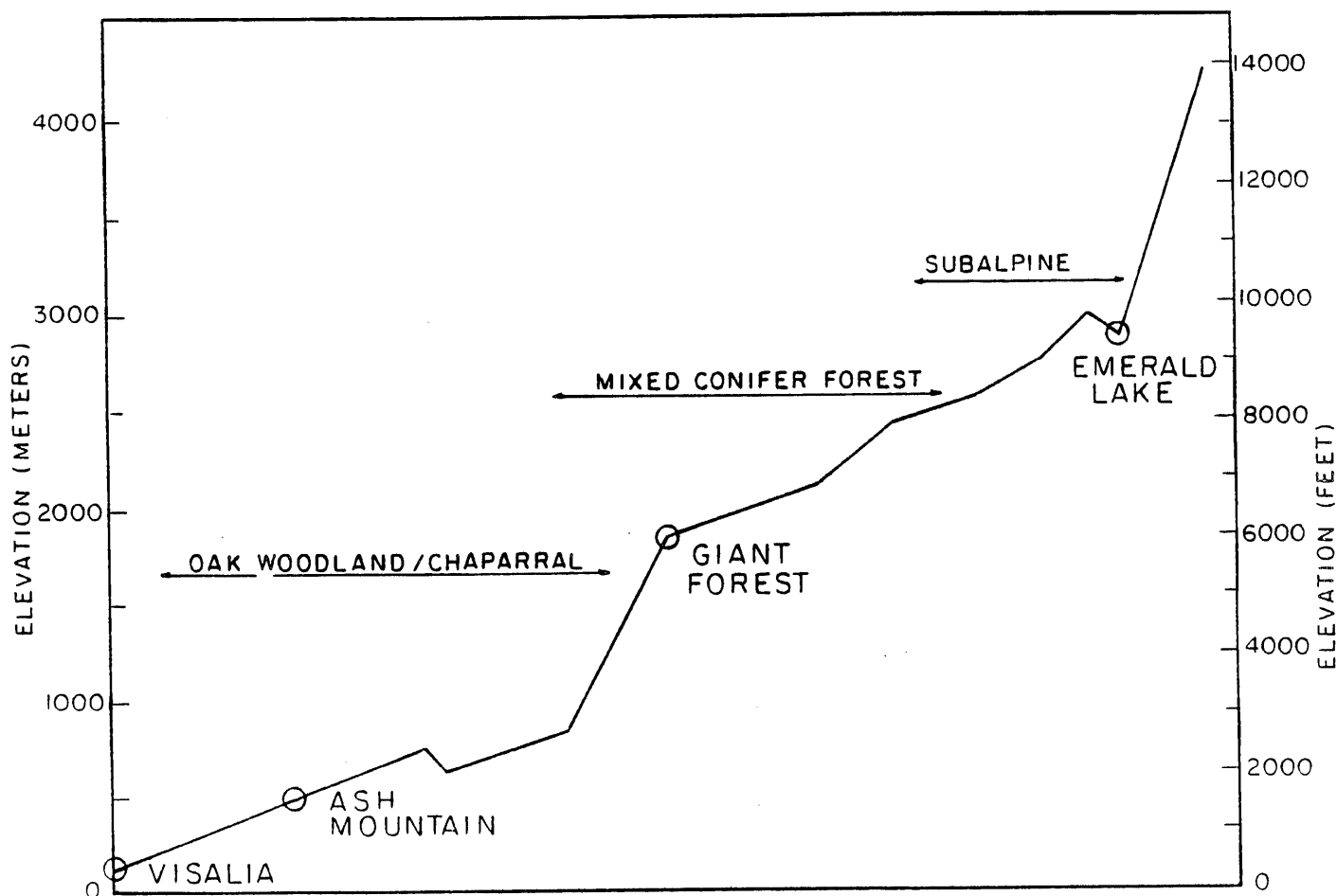
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PROJECT SUMMARY

The report describes a 3-year project by the Air Quality Group of Crocker Nuclear Laboratory to monitor atmospheric particles and ozone in Sequoia National Park.

In support of the acid deposition effects programs at Sequoia, we made extensive measurements of particulate matter from summer 1985 through 1987. We took continuous samples at three elevations [608 m (2000 ft), 1946 m (6400 ft), 3040 m (10000 ft)] in up to nine size ranges.

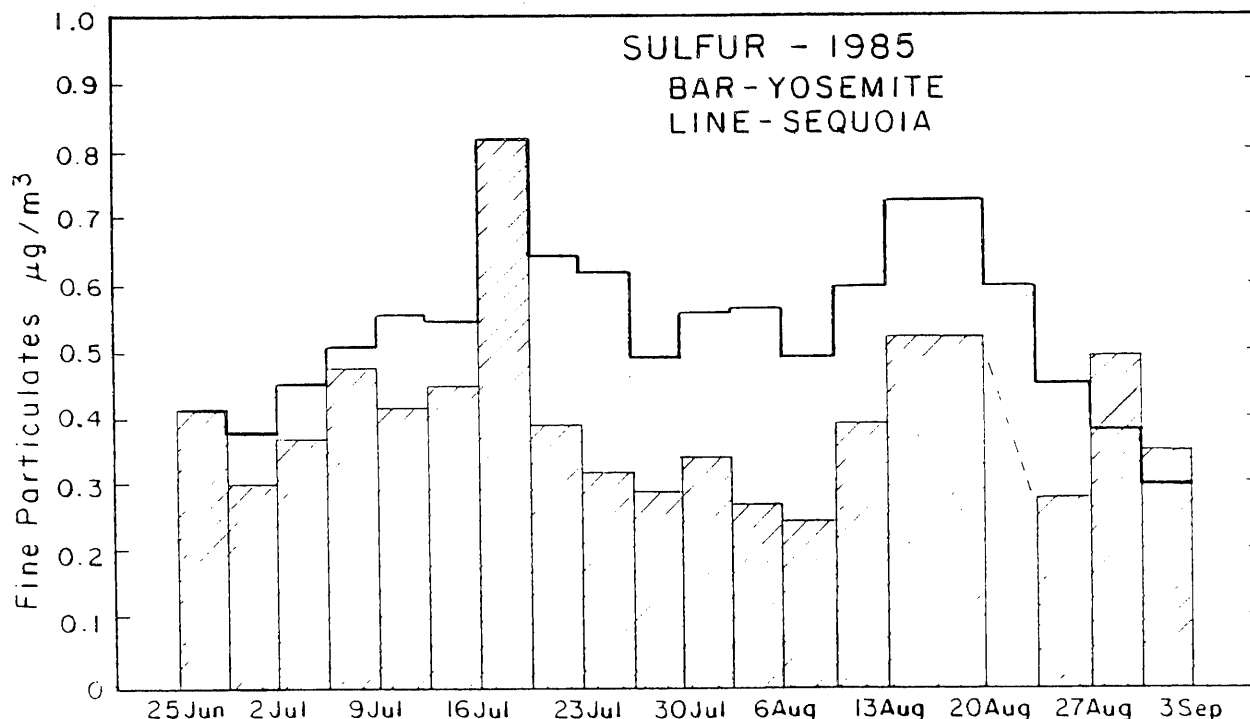


Almost 4000 analyses were then done for mass, carbon soot, hydrogen, and elemental species up through lead. The data were correlated with local and synoptic meteorology, known elemental source signatures, and dry deposition and wet deposition measurements made in the four major rain events during summer 1985.

The original objectives of this project were (1) to characterize the composition of fine particles and to determine what material is available for wet and dry deposition by measuring particulate concentrations by element with detailed size and time resolution; (2) to determine how particulate concentrations vary as the meteorology changes; (3) to determine the extent of transport of particulate pollutants from the San Joaquin Valley by comparing elemental concentrations measured at three elevations with sufficient time resolution to look at transport; and (4) to provide convenient time plots and other visual representations of particulate concentrations compared to concurrent projects on the effects of wet and dry deposition and compared to studies of meteorology and gases. In 1986, these objectives were extended to include development of a solar-powered ozone monitoring system for high altitude ozone measurements intended for use in 1987; improved particulate size data at Emerald Lake; and year-round comparisons of Sequoia National Park to the National Park Service IMPROVE site at Turtleback Dome, Yosemite National Park. Lack of summer precipitation at the Giant Forest site prevented a study of wet deposition events.

The results are

1. The Yosemite National Park sites are well correlated with the Sequoia National Park site at Giant Forest at the same elevation on a north-south gradient, $r^2=0.6$, with the three-year comparison having higher concentrations of most particles at Giant Forest by a ratio of 1.6 ± 0.2 . Nickel, however, a tracer of fuel oil combustion, is 2 to 3 times higher at Sequoia than Yosemite, indicating admixtures of air from the nickel rich aerosols of the southern San Joaquin Valley.

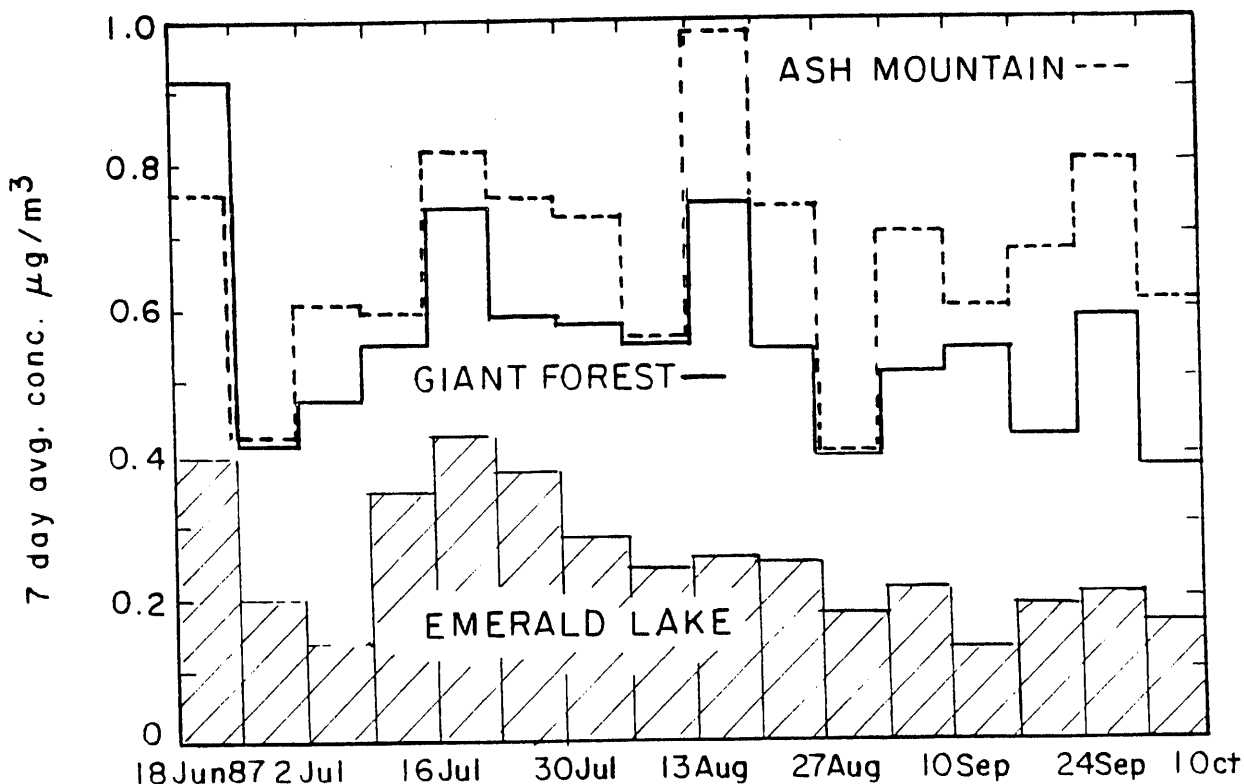


This result has an important implication in that the new NPS IMPROVE site at Turtleback Dome can provide data relevant to large areas of the western Sierra slope around 1824 m (6000 ft) elevation, with only modest scaling factor corrections for sites south of Yosemite.

The results also showed sharply lower levels of sulfate north of Sacramento, reduced by a factor of 2 or more, which may be reflected in acidic deposition at sites east of the Sacramento Valley.

2. There is also an abrupt reduction of all particulate pollutants at Sequoia and Yosemite National Park [~ 1824 m (~ 6000 ft) elevation] about November 1 of each year, and a rapid rise in pollutants after April 1. During the winter, particulate air quality is excellent, comparable to the cleanest sites in the United States. This result is unique to these sites, and is due to the strong winter inversions keeping a lid on San Joaquin Valley pollutants at about 608 m (2000 ft) elevation.
3. Summer air quality at Sequoia National Park from 608 m (2000 ft) to above 1824 m (6000 ft) is dominated by transport of aerosols and ozone from the San Joaquin Valley with little dilution in concentrations.

Somewhere above 1824 m (6000 ft), but below 2736 m (9000 ft), air quality sharply improves, with major reductions in fine particles and ozone. Further, the synoptic and diurnal correlations of pollutants weaken, indicating some decoupling of air quality from the San Joaquin Valley's terrain-dominated, diurnal wind patterns.



4. On several occasions in 1985, but rarely in 1987, transport of air and pollutants was observed from the east, generally with sub-tropical air masses and thunderstorms. These events resulted in higher levels of wet acidic deposition than did storms from the west.
5. Particulate matter present at Giant Forest was derived largely from the San Joaquin Valley, but because coarser particles were lost during transport, the particle size ranges were modified to finer modes. This has direct implications for dry deposition rates. It also decreases the buffering by natural soil particles (generally larger size) of acidic dry deposition.
6. Regular transport of ozone from the San Joaquin Valley to Sequoia was observed on almost every day. The concentrations of ozone at Visalia, Ash Mountain, and Giant Forest were practically identical during daylight hours. At night, elevated ozone concentrations persisted at Ash Mountain and Giant Forest, while concentrations on the valley floor fell to low levels at Visalia, probably due to scavenging.
7. Ozone concentrations were low at Emerald Lake, day and night, with only a slight indication of diurnally transported ozone in the early evening.

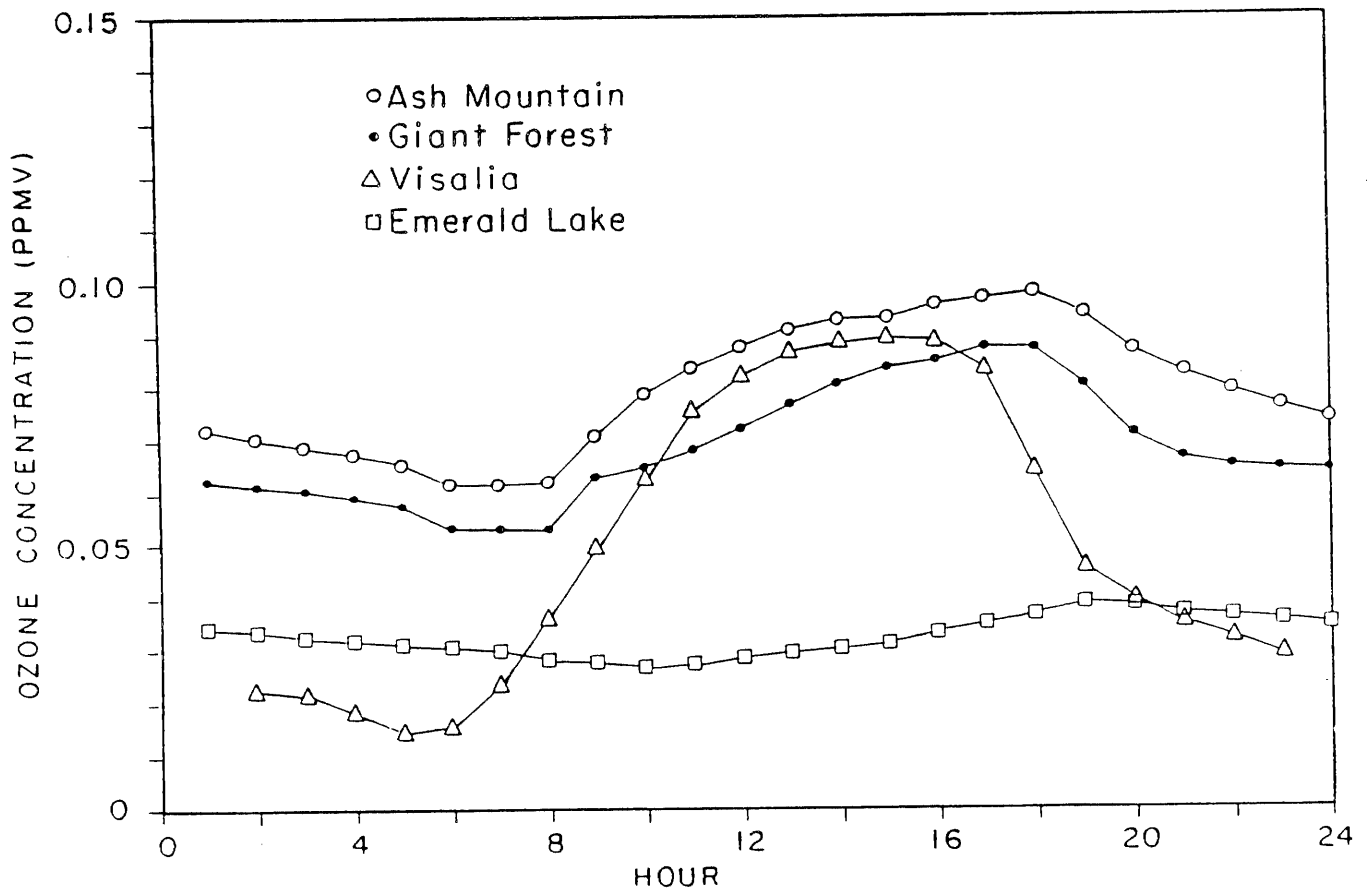


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INTRODUCTION

An area of unique and worldwide biological interest, Sequoia National Park contains a range of ecological communities spanning elevations from 608 m (2000 ft) to 4408 m (14500 ft) (Figure 1) and including chaparral, coniferous forest, alpine ecosystems, besides of course rare stands of "Sequoia Gigantea." The park straddles California's Sierra Nevada mountain range east of the San Joaquin Valley, an area characterized by high ozone and suspended particulate matter from local and distant sources. Sequoia is an important acid deposition monitoring site in California. Because the Sierra ecosystem is close to relatively elevated levels of air pollution in the San Joaquin Valley, efforts have been made to document the effects of air contaminants, through wet and dry deposition, on the forests of the western Sierra slope. For several years, Sequoia has been the site of intense research, funded by the California Air Resources Board (CARB), the National Park Service, and others, to measure and understand the impacts of acid deposition and other air pollutants on the park's ecosystems. Rainfall with a pH as low as 3.5 has been measured in the park (CARB 1986). Ozone is held responsible for widespread injury to Ponderosa and Jeffrey pines, as well as other plant species (Duriscoe 1987). Park visitors are aware of the significant impact of visibility-reducing particles on scenic vistas.

During a three-year period (1985-1987), the Air Quality Group, Crocker Nuclear Laboratory, University of California, Davis, monitored atmospheric particles and ozone as part of the air pollution research program at Sequoia under contracts from the California Air Resources Board.

The particulate concentration data that the Air Quality Group accumulated are essential for two reasons: 1) They indicate the potential for dry deposition of particles. The dry summers of the Mediterranean climate of California make dry deposition a major mechanism for particle removal at Sequoia, accounting for perhaps 70 to 90% of the total deposition during the summer. 2) Particulate data with sufficiently high time and size resolution can provide valuable answers to questions on the scavenging processes for wet deposition. For example, what happens to the particulate levels when a front approaches? Is the air cleaned so that the rain has little particulate material to deposit, or do the levels remain at the average value? What happens to the particles (around 0.5 μm) in the size range that tend to be incorporated into cloud water droplets?

The overall objectives of the 1985 study were to

1. Characterize the particulate composition of fine particles by determining the concentration of all elements from hydrogen through lead.
2. Determine what material is available for wet and dry deposition by measuring particulate concentrations by element and size.
3. Determine how particulate concentrations vary with time as the meteorology changes. This will be viewed by elemental species and particle size.
4. Determine the extent of transport of particulate pollutants from the San Joaquin Valley by comparing elemental concentrations measured at three elevations with sufficient time resolution to look at transport.

5. Provide convenient time plots and other visual representations of particulate concentrations compared to concurrent projects on the effects of wet and dry deposition and to studies dealing with meteorology and gases.

The results for 1985 are published in the report Particulate Monitoring for Acid Deposition Research at Sequoia National Park, California, May 1986. A continuation study was mounted in 1987-1988 to resolve questions raised by the 1985 data and extend the project to ozone monitoring at sites lacking 110v power. The objectives of the 1986-1987 study were to

1. Characterize the composition of fine particles by determining the concentration of all elements from hydrogen through lead, now in association with wet deposition monitoring (performed by the ARB) and ozone monitoring.
2. Monitor particles at two sites, one at high-elevation and one at mid-elevation, to further characterize and distinguish pollution impacts at the different elevations.
3. Characterize the particulate and precipitation chemistry of different storm types.
4. Further characterize pollutant pathways into the Sierra, by interpretation of pollutant concentrations and meteorology on local and synoptic scales.
5. Establish regional pollutant gradients in the Sierra, by comparing particulate concentrations at Sequoia and Yosemite over a year-long sampling cycle.
6. Develop and test a solar-powered ozone monitor for use in remote locations, and to use this monitor for ozone measurements at high elevations in the Sierra.

Figure 1 shows the location of Sequoia National Park, and Figure 21 shows our monitoring sites. The Ash Mountain site was located at an elevation of 608 m (2000 ft) near the western park boundary. The Giant Forest site was located at an elevation of 1915 m (6300 ft) at Lower Kaweah near the western edge of the Giant Forest. During the summers of 1985 and 1986 our site near Emerald Lake was on the ridge between Emerald and Pear Lakes at 3040 m (10000 ft) ("ridge" site). During the summer of 1987 a more accessible location below Emerald Lake was chosen at an elevation of 2736 m (9000 ft) ("valley" site). All four of these sites were in the same watershed. Emerald Lake drains into the Marble Fork of the Kaweah River. The Giant Forest site was at the edge of the canyon of the Marble Fork, and the Ash Mountain site was along the Kaweah River, downstream of the Marble fork's junction with the main river.

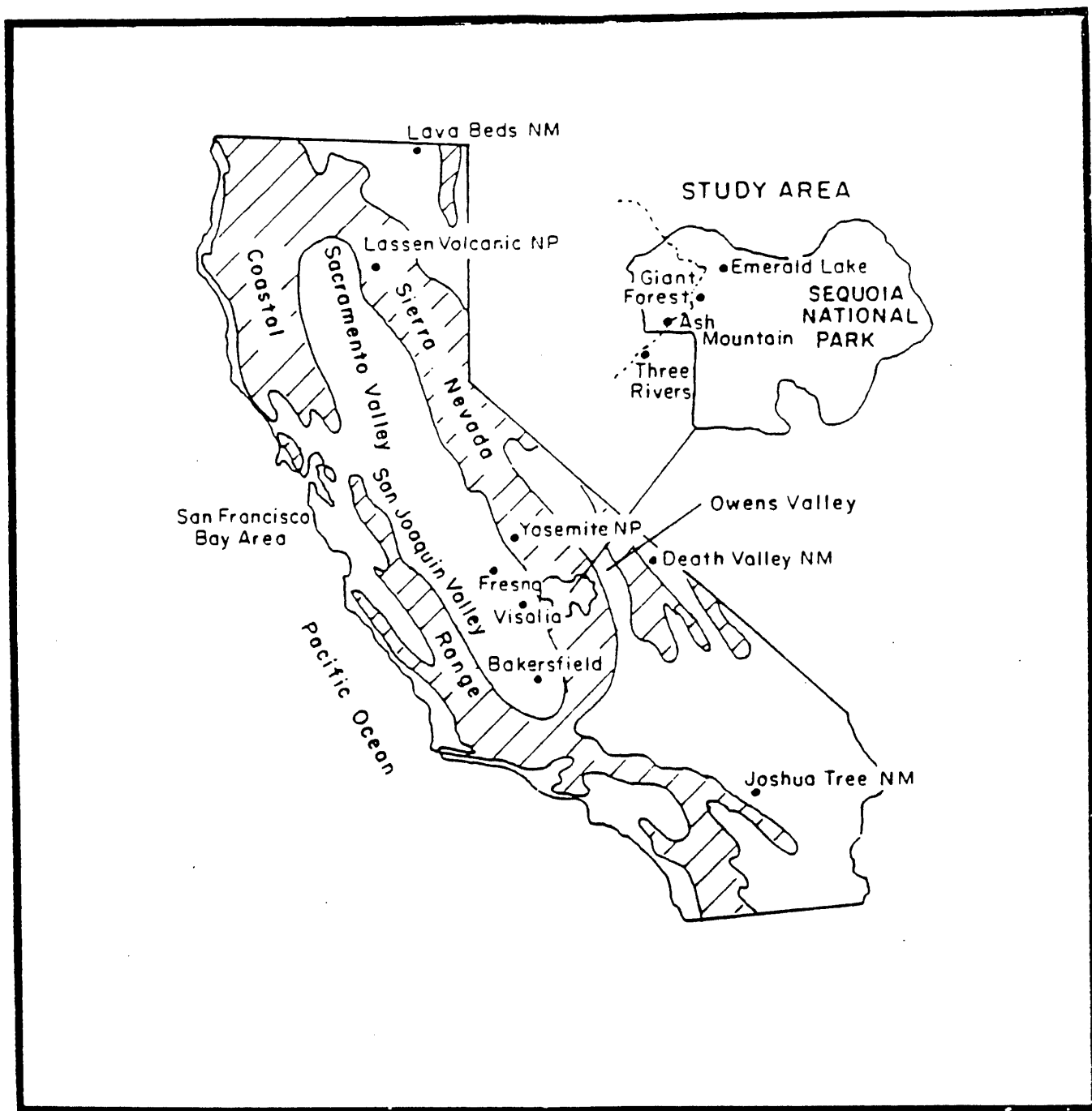


Figure 1: Study sites

This report, which describes our Sequoia air quality monitoring during 1985 to 1987, begins with background discussion of the air pollution meteorology of Sequoia and the surrounding area. The body of the report is divided into two sections: a discussion of atmospheric particle monitoring and results, and a discussion of ozone monitoring and results.

METEOROLOGY OF SEQUOIA NATIONAL PARK

Wind patterns in mountains during the summer are complex because of the rugged terrain and intense daytime solar radiation. Topographic features also have a strong influence on mountain meteorology. Important topographic features surrounding Sequoia National Park include the San Joaquin Valley, the Coast Range, and Pacific Ocean to the west, and the Owens Valley, White Mountains, and Great Basin to the east (see Figure 1), in addition to the influences of the Sierra Nevada among which the park is set.

During the summer months, the predominant surface wind direction in the San Joaquin Valley is from the northwest or "up-valley" from Stockton towards Bakersfield (Hayes et al. 1984). This flow is a result of the land-sea breeze, the Pacific coast summer monsoon, and the Sierra Nevada (Schroeder et al. 1967).

In Fresno, the morning surface flow is frequently from the south or from the west (toward the Sierra) and characterized by light wind speeds. By afternoon, however, the winds are from the northwest at 5-10 m/sec, peaking around 1600 PST. The strongest wind speeds occur aloft and are commonly observed near midnight due to the formation of a low-level nocturnal jet (Smith et al. 1981). This jet results partly from the nocturnal inversion which forms almost every day of the year in the San Joaquin Valley (Lorenzen 1979). The average height of the jet's maximum intensity is approximately 300 m (985 ft). The jet is less developed or absent during synoptic disturbances, or when the marine air inversion is deep enough to allow the cool marine air to flow over the Coast Range into the San Joaquin Valley (Willis and Williams 1972).

The southerly flow observed in the morning hours in Fresno results from a wind pattern referred to as the "Fresno Eddy," observed to occur regularly during the summer (Smith et al. 1981; Blumenthal et al. 1985). The vertical extent of the Fresno Eddy is typically 1000 m (3280 ft). Beginning close to midnight, it is observed in Fresno by 0800 PST the following morning (earlier in Visalia). The eddy center is generally located west of Visalia with Fresno being the northern limit, although it can extend further north. Usually restricted to the eastern side of the valley, the eddy causes a funneling of the northwesterly flow down the western side of the valley in the morning hours. Its wind speeds are generally less than 5 m/sec. The days during which the eddy is less developed or absent are characterized by synoptic disturbances causing instability.

During a study in 1979, both the Fresno Eddy and the nocturnal jet occurred approximately 80% of the time in July and September (Smith et al. 1981). The jet provides a mechanism to transport air pollutants rapidly from the northern end of the San Joaquin Valley (the San Francisco Bay area), to the southern end of the valley. The daytime up-valley flow also contributes to this pollutant transport. The Fresno Eddy may be a significant mechanism for transport of pollution from the oil fields at the southern end of the San Joaquin Valley to the central part of the valley. The analysis of Ewell et al. showed that "August, 1985 was not markedly different from other years in the record." Thus, data from the 1985 period should be considered roughly typical, although the remnants of a hurricane introduced moisture around August 17, 1985.

Topographic winds in the Sierra include daytime up-valley and upslope winds or nighttime down-valley and downslope winds. The general characteristics of slope, valley, and mountain winds are described in the literature (see, for example, Whiteman 1980; Orgill 1981). During the daytime, flow in the mountains is directed upslope and up-valley ("valley" wind), usually beginning a few hours after sunrise and ending near sunset. During the nighttime, the flow is reversed to downslope and down-valley ("mountain" wind). These winds recur often despite changing winds at higher elevations (Ewell et al. 1988). The basic valley, mountain, and slope flows interact with other commonly observed wind flow patterns in complex ways, as summarized in Ewell et al. (1988). As an example, the following figures show the regularity of the topographic winds at Sequoia. Figure 2 shows the diurnal wind direction near Ash Mountain in July and August 1985, while Figure 3 shows the wind speed at Elk Creek. The extraordinary regularity can be summarized in Figure 4, showing mean transport along a 1090--2890 axis aligned with the topography.

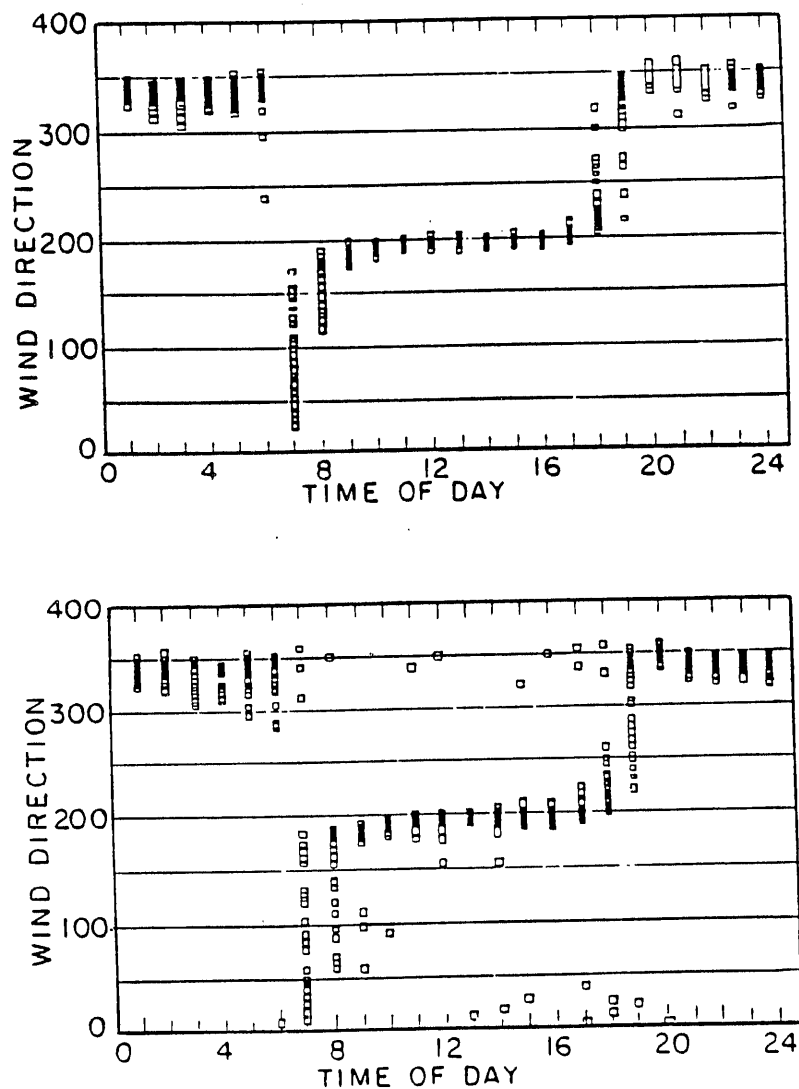


Figure 2: Diurnal wind direction, near Ash Mountain, July/August 1985

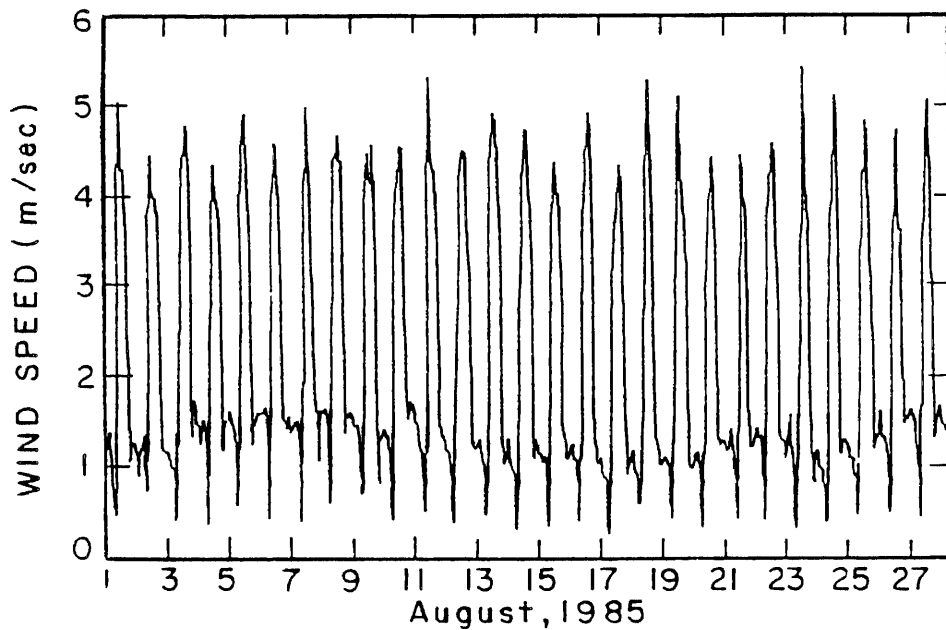


Figure 3: Hourly wind speeds at Elk Creek, Sequoia NP, August 1985

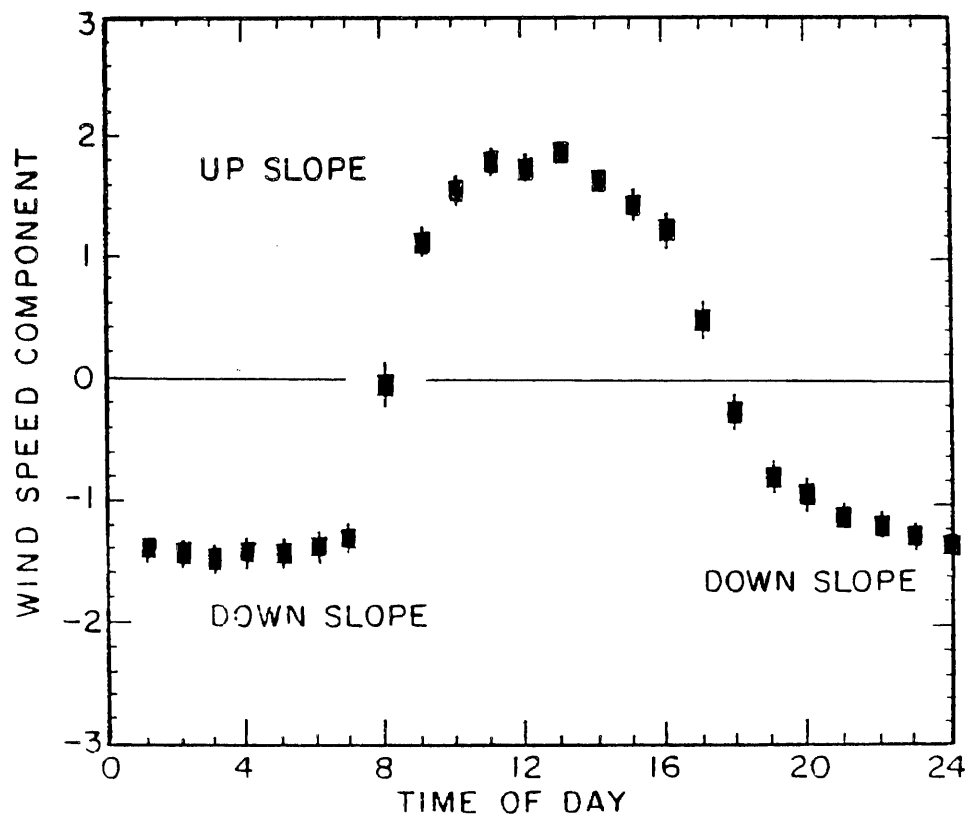


Figure 4: Mean diurnal wind speed at mid-elevation station, Sequoia NP

In addition to the phenomena discussed above, synoptic scale flows determine the long range transport of pollutants to Sequoia, including transport from the southeast. Synoptic scale meteorological features are seen clearly, especially above 3000 m, and they are irregular in their occurrence (Ewell et al. 1988). The pilot balloon plots of Ewell et al. (1988) revealed three wind regimes.

The first is the lower, boundary-layer flow system. This regime is dominated by a very regular oscillation of upslope and downslope winds controlled by the diurnal variation of solar heating of the Sierra slopes. Pilot balloon data were used by Ewell et al. to estimate the depth of the topographic winds. In comparing the three mountain sites, they found that the upslope/downslope regime is both deeper and more intense at Ash Mountain than at the higher locations. This is true for both the upslope and downslope winds; in each case the winds at Ash Mountain are usually stronger and extend to greater heights than at Wolverton and Emerald Lake. An example appears in Figure 5 (Ewell et al. 1988). The aerosols present at Ash Mountain should clearly reflect the Central Valley atmospheric boundary layer, but the situation is less certain at 2000 m (6560 ft) elevation at Giant Forest (Wolverton), and even less so at Emerald Lake.

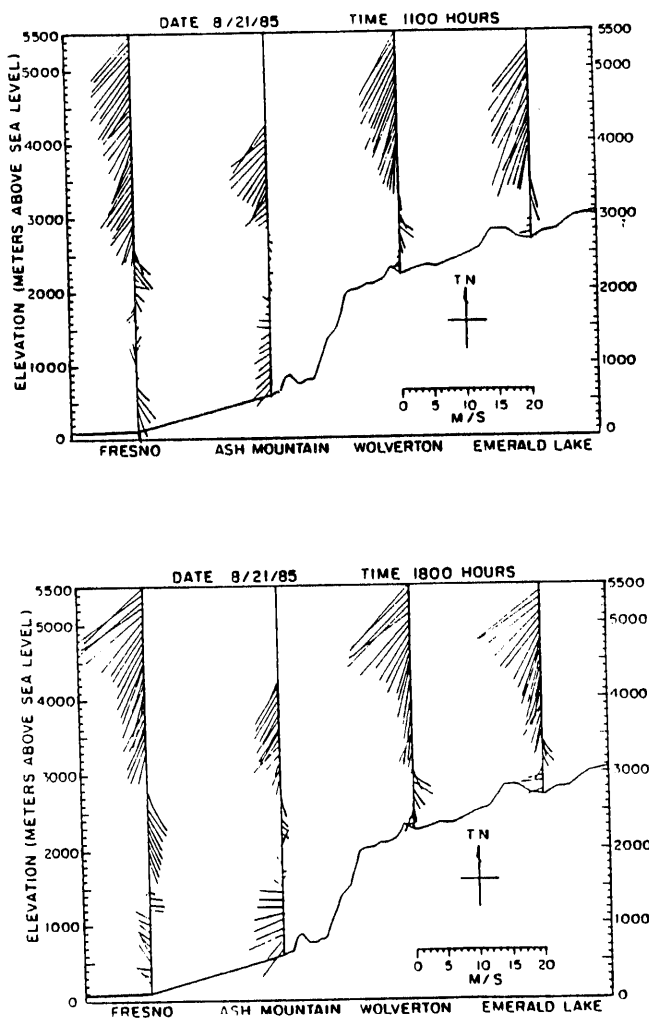


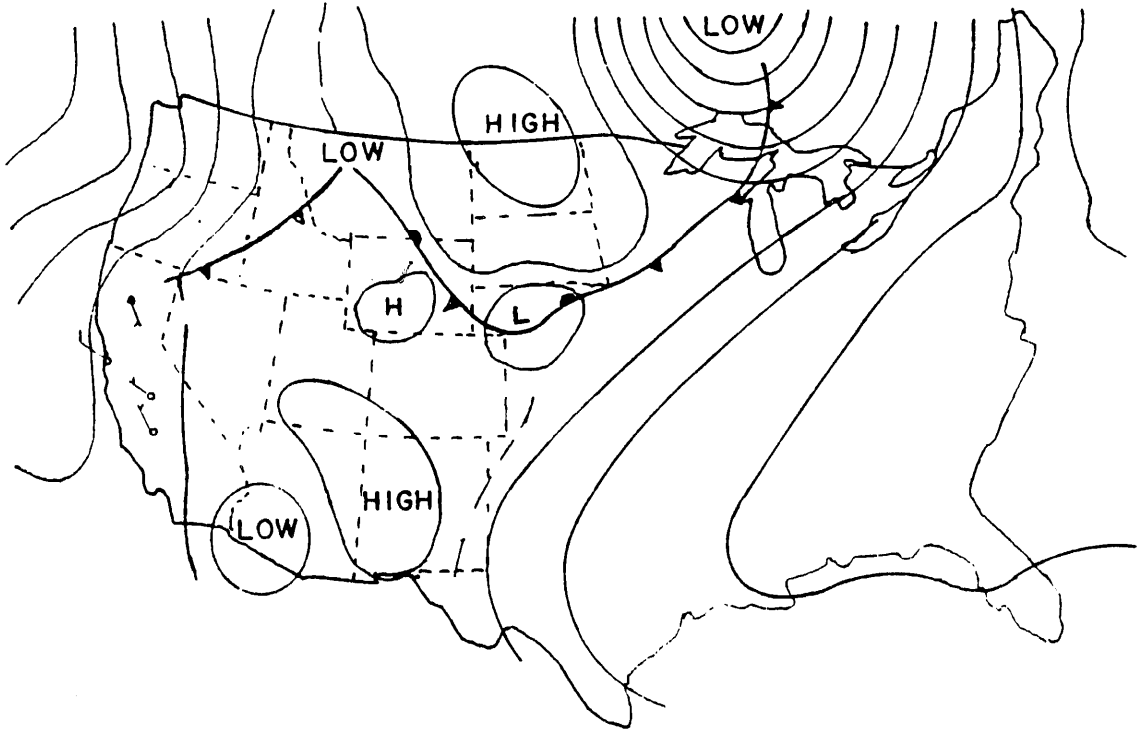
Figure 5: Pilot balloon wind profiles for August 21, 1985

The second meteorological regime is the meso-scale San Joaquin Valley wind system. This circulation sweeps up the valley in a northwesterly current which reaches its maximum strength in late evening. The valley circulation has two specific features which may be significant to air quality meteorology in Sequoia. One is the nocturnal jet which is strongest about midnight, according to (Smith et al., 1981). The jet may be an efficient means to transport pollution from Central California to the southern San Joaquin area. The second feature of interest is the Fresno Eddy. This flow feature may be a significant mechanism for transport of pollution from the oil fields of Kern County to the Sequoia area.

The third regime is associated with synoptic-scale variation. These fluctuations appear most clearly at upper levels and occur irregularly. The synoptic scale controls long-range transport, particularly the transport of sulfur-rich air from regions to the south of Sequoia. This was illustrated in the elevated sulfur episode of June 22-28, 1985. Meteorological maps from June 22-28 have been used for analysis. The charts include surface maps, 500 mb charts, the highest and lowest temperature charts, and precipitation areas.

On the surface, the major feature consisted of a cold front extending from Montana into northern California, and a trough from eastern Utah into southern Colorado. The trough was an extension of the surface low pressure center. There was little temperature and moisture contrast across the front in northern California. At 500 mb a mid-level jet was located in northern Oregon, Idaho, and Wyoming along the northern side of the surface front. There was a well-developed northwesterly flow which induced a southward swing of the surface front. On June 24, 1985, the surface chart showed a well-developed strong trough on the western part of the United States (Figure 6). The advection of cool, dry air associated with strong northerly winds in the middle troposphere and the northward movement of a warm, moist air mass in the low troposphere (surface low pressure) could create favorable conditions for convection thunderstorms over California. During the next few days, the previous trough moved eastward, and the strong trough over the Pacific Ocean caused vigorous southwesterly flow over the western part of California.

June 23, 1985



June 24, 1985

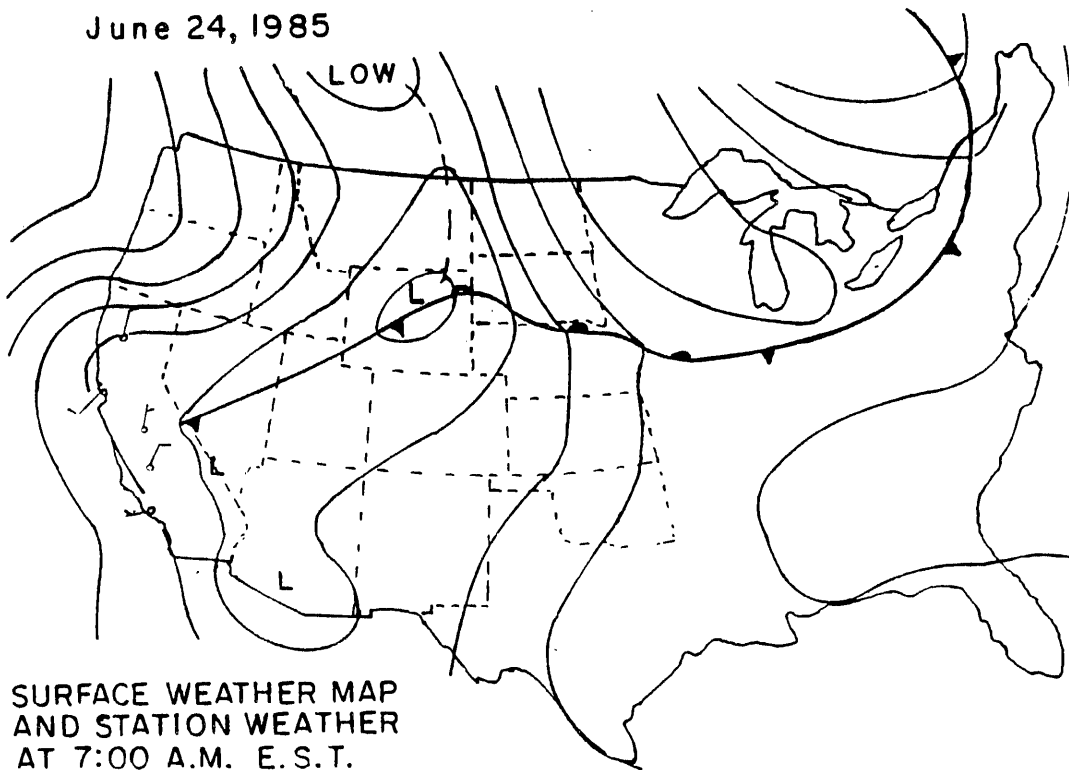


Figure 6: Synoptic chart for the USA, June 23-24, 1985

The effect of the passage of the cold front is clear in the wind direction at Fresno, the relative humidity at Elk Creek (Figure 7), and the fine sulfur at Ash Mountain (Figure 8). The cold front led to large sulfur peaks on both June 24 and June 25, 1985 at midnight and cleared up during daytime hours. Since the front generated southerly winds, relatively high sulfur concentrations can be associated with sources south of Sequoia, such as the southern San Joaquin Valley.

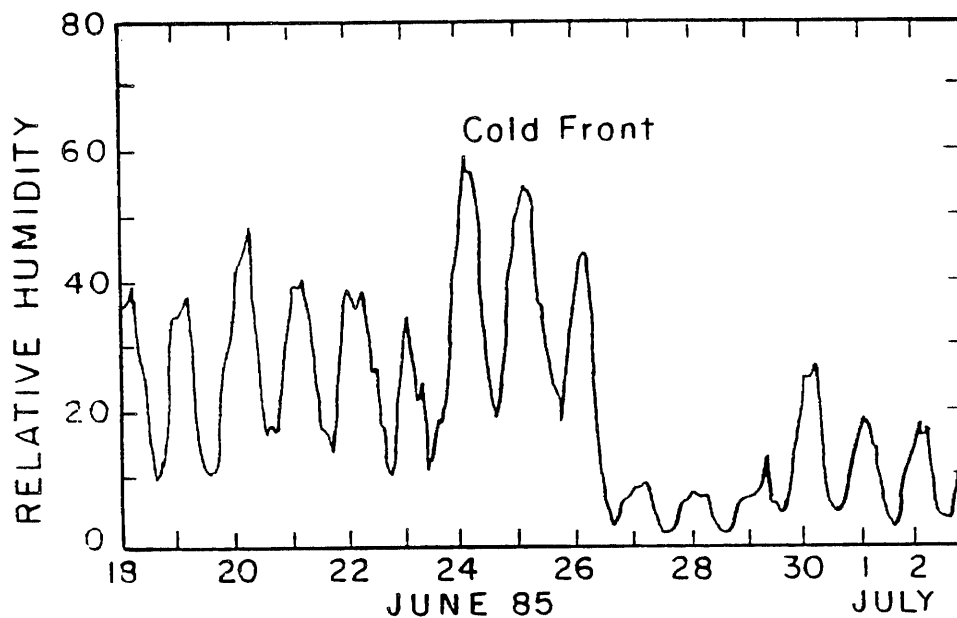


Figure 7: Relative humidity at Elk Creek, Sequoia NP, June 1985

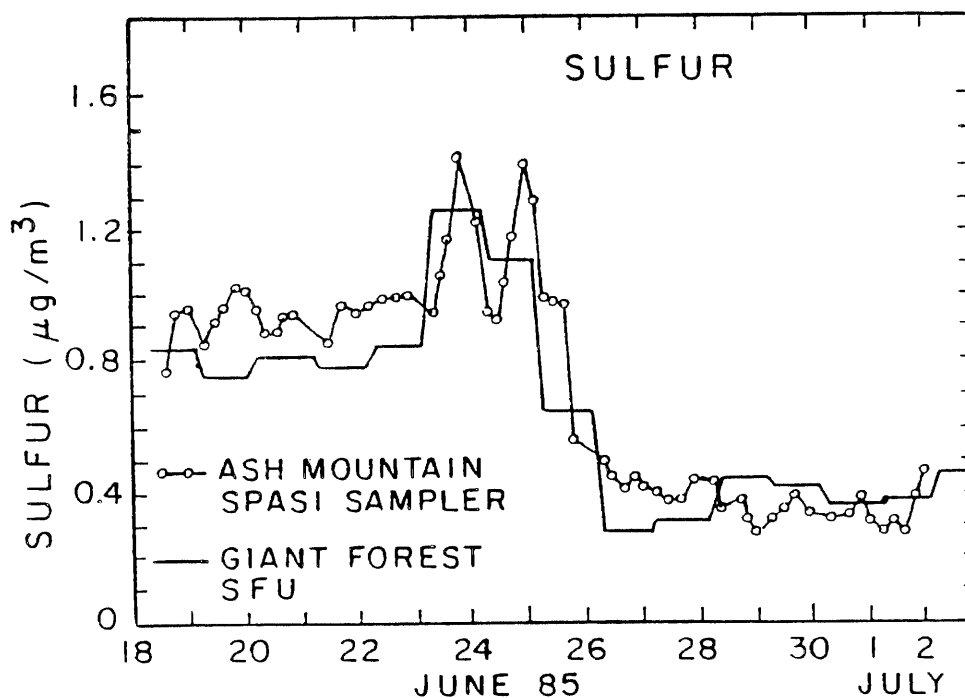


Figure 8: Fine sulfur at Giant Forest and Ash Mountain, June 1985

These circumstances also indicate the relative strength of the Fresno Eddy versus synoptic meteorology in pollutant transport. Interestingly, neither fine potassium, a smoke tracer, nor fine silicon, a soil tracer, responded significantly to the cold front, probably because there are sources of soil and smoke all over the San Joaquin Valley (figures 9, 10). But the sulfur sources are more uniquely found south of Sequoia, and so responds to frontal passage.

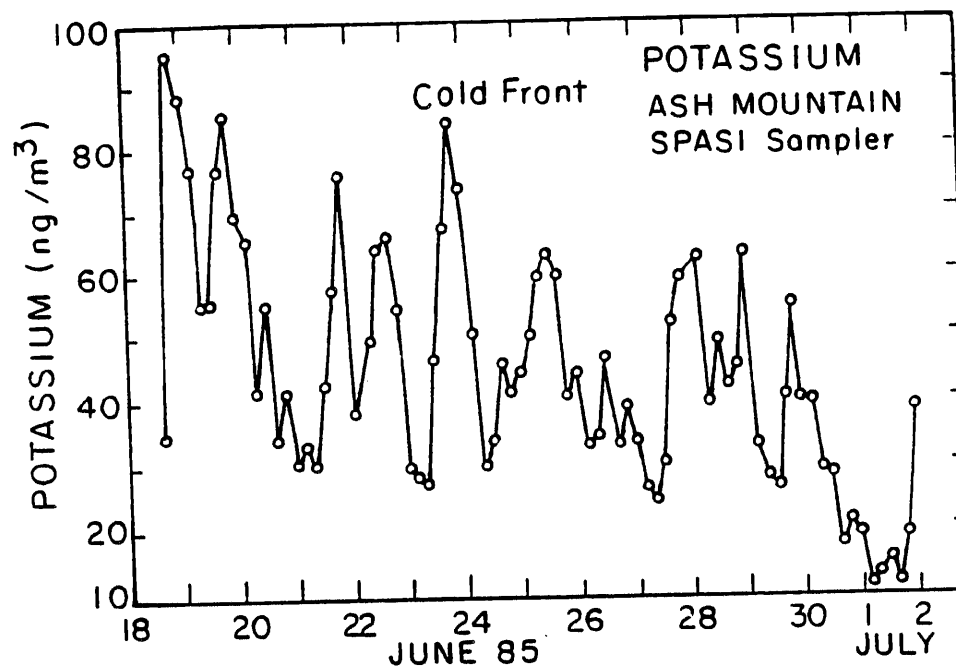


Figure 9: Potassium at Ash Mountain, June 1985

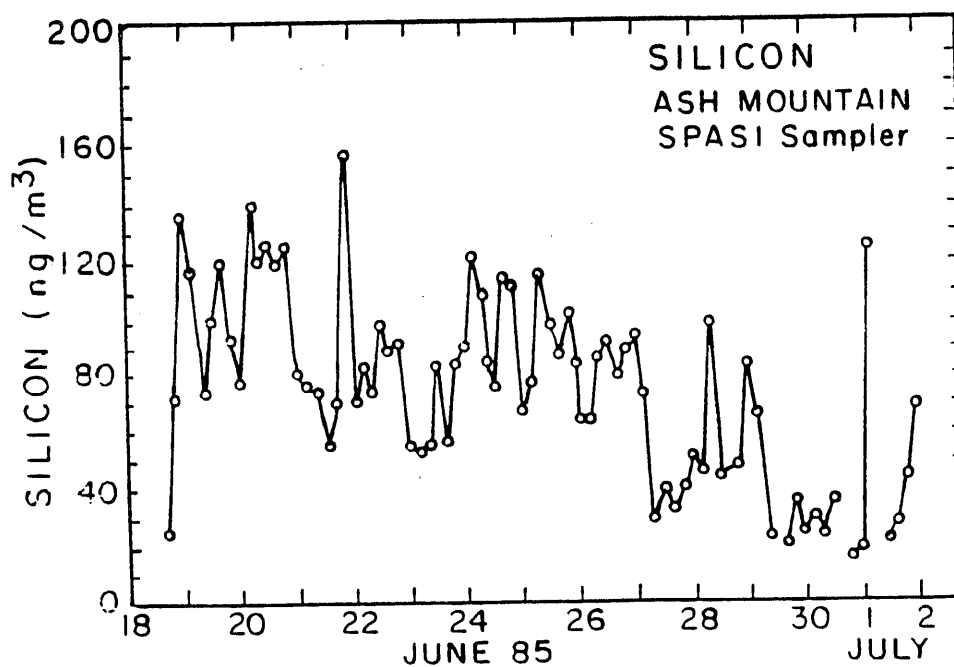


Figure 10: Silicon at Ash Mountain, June 1985

The meteorology of the Sequoia sites and much of the western slope of the Sierra Nevada, east of the San Joaquin Valley, results in potential transport of pollutants from four major sources (listed roughly in frequency of occurrence): (1) Local San Joaquin Valley sources dominated by agricultural and automotive sources; (2) Southern San Joaquin Valley sources via the Fresno Eddy; (3) Bay Area sources via the low level nocturnal jet. Each of these sources results in a mixture of aerosols and gases within the atmospheric boundary layer which are then transported to higher elevations [> 2000 m (6560 ft)] by the diurnal upslope winds that occur almost every summer day (Cahill 1985). And (4), Southern California Desert and Arizona sources, with transport up the eastern Sierra Nevada, often including subtropical moisture and thunderstorms.

Synoptic weather fronts and strong radiation inversions--two other noteworthy meteorological conditions--are important, especially during fall, winter, and spring. Synoptic weather fronts from the mid- and north-Pacific, while relatively uncommon in summer, are common during the remainder of the year. These generally result in improved air quality at Sequoia. Finally, the strong radiation inversions in the fall and winter restrict pollutants in the valley to about the 500 m (1640 ft) level and result in sharply improved air quality from about mid-October to early May.

The complicated meteorological conditions in the western Sierra slope compound the problems of forming causal connections between pollutant sources, air quality, dry and wet acidic deposition, and damage to vegetation.

PARTICULATE STUDIES

Instrumentation and operations

We employed various sampling instruments and analytical methods. Particulate matter was collected by 5 different instruments (SFU, solar-powered SFU, DRUM, SPASI, and VI) which classified particles by size. The resulting samples were analyzed for mass, carbon soot (LIPM), and constituent elements (PIXE, FAST, and PESA). Table 1 summarizes our air quality monitoring activities in Sequoia by year and site. The sampling periods also appear in Figure 11.

A standard Environmental Protection Agency (EPA)-National Park Service (NPS) SFU sampler was borrowed from the NPS for service at Giant Forest. This type of sampler has been operated at 31 parks and monuments since 1979 under formal third-party quality-assurance protocols and so insures direct comparability of Sequoia Giant Forest data to data for all NPS and California sites operated by the Air Quality Group. For quality assurance, an Air Resources Board virtual impactor (VI) was also located at the Giant Forest site. Average fine mass agreed $\pm 10\%$ between the VI and the SFU, which was also the result of the aerosol sampler intercomparison at the Desert Research Institute, June 1984. (Mathai, 1986).

In order to obtain high resolution data on particulate size and short-time (4-hour) resolution on particulate matter vs. time, a Davis Rotating-drum Unit Monitoring (DRUM) sampler was built at UCD and deployed at Sequoia National Park. The unit operates continuously for two weeks at a time. Data from this unit were the key to unlocking the remarkable diurnal size/composition variations at Giant Forest. The DRUM unit participated in the Desert Research Institute study (which compared particle sampler side by side), with excellent agreement for elemental species such as sulfur. In addition, this unit has provided significant insights into aerosol physics and chemistry as part of the RESOLVE and SCENES studies of the California-Arizona deserts, and the NPS-Grand Canyon Study, delivering sensitivity to a few nanograms/m³). It is accurate to better than $\pm 10\%$, in 4-hour size increments and 8 analyzable size cuts. The size cuts of the DRUM used in 1987 were 13 μm to 8.5; 8.5 to 4.3; 4.3 to 2.1; 2.1 to 1.15; 1.15 to 0.56; 0.56 to 0.34; 0.34 to 0.24; 0.24 to 0.07; 0.07 to 0 (afterfilter). A single stage rotating drum sampler capable of being operated using solar power, the Solar Powered Air Sampling Impactor (SPASI), was used at most sites and provided high time resolution for particulate elements below 2.5 μm .

Table 1. Summary of air quality monitoring activities and air quality monitoring sampling periods

<u>Year/ Site</u>	<u>Sampler</u>	<u>Sampling Period</u>	<u>Protocol</u>
1985/ Ash Mountain	SPASI SFU	6/18-10/8 6/18-10/8	Continuous 1-3 day and 1-4 day samples per week
Giant Forest	DRUM SFU VI	6/18-10/8 6/18-10/8 7/9-10/8	Continuous 7-24 hour samples per week 7-24 hour samples per week
Emerald Lake	SPASI SolarSFU	6/25-10/10 6/18-10/10	Continuous Changed weekly
1986/ Giant Forest	SFU SPASI	6/17-12/31 6/17-9/30	7-24 hour samples per week (plus intensives) Continuous
Emerald Lake	SPASI Ozone	6/20-9/30 9/12-9/30	Continuous Continuous (No useable data)
1987/ Giant Forest	SFU DRUM	1/1-11/3 7/21-9/24	2-24 hour samples per week (plus intensives) Continuous 2 afterfilters per week
Emerald Lake	SolarSFU Ozone	7/5-9/2 7/26-9/24	4 Changed weekly plus intensives Continuous

SITE/ INSTRUMENT	1985	1986	1987
ASH MOUNTAIN			
SFU	████		
SPASI	████		
GIANT FOREST			
SFU	████	████████	████████████
SPASI		████	
DRUM	████		██
VI	████		
EMERALD LAKE			
SOLAR SFU	████		████
SPASI	████	████	
OZONE		█	██

Characteristics of Central Valley Aerosols

Our meteorological analysis indicates that aerosols of the San Joaquin Valley will be regularly transported into Sequoia on the strong diurnal wind patterns. Their characteristics will be a major, if not the major, predictor of aerosol composition in the biologically sensitive areas of the park. We will now examine the characteristics of the San Joaquin Valley aerosols as they may bear upon the results of ambient air sampling in the park itself.

Data are available at sites within the San Joaquin Valley, as reported quarterly by the California Air Resources Board (CARB 1986). Two sites, Visalia and Modesto, provide data that may be representative of source regions close to the western Sierra slope.

Figure 11 shows the PM10 values at these sites for March through September 1987. Earlier high-volume filter samplers (Hi-Vols) lacked the 10 μm inlet cut and thus provided data even more influenced by local large soil particles than the new PM10 units. Three points should be noted. First, the mean summer PM10 values, around 40 $\mu\text{g}/\text{m}^3$ at Modesto and 70 $\mu\text{g}/\text{m}^3$ at Visalia, are quite large, indicating a potential for significant aerosol transport into the parks. Second, the two sites, although separated by over 160 km (100 miles), do possess significant correlation, most likely from the influence of synoptic meteorological systems. Third, Visalia levels are much higher than Modesto ones, although Visalia is a smaller urban area.

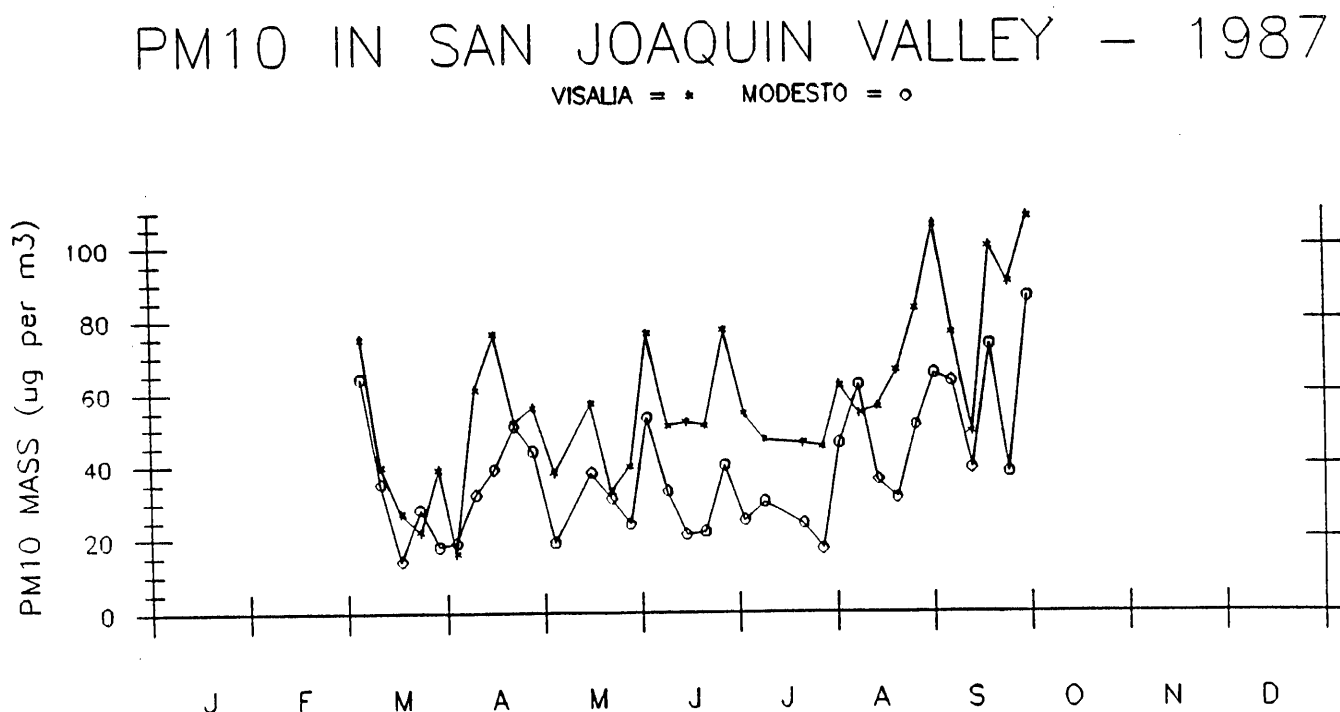


Figure 11. PM10 in San Joaquin Valley, 1987

Figure 12 shows sulfate at the two sites for 1987. Values are a small fraction of PM10 values, the sites are now very similar in mean levels, and intersite correlations are much higher. Clearly, sulfate is more regional in nature than PM10 mass. At Visalia, which is closest to Sequoia, sulfates represent about 5% of PM10 mass.

SULFATE IN SAN JOAQUIN VALLEY — 1987

VISALIA = * MODESTO = o

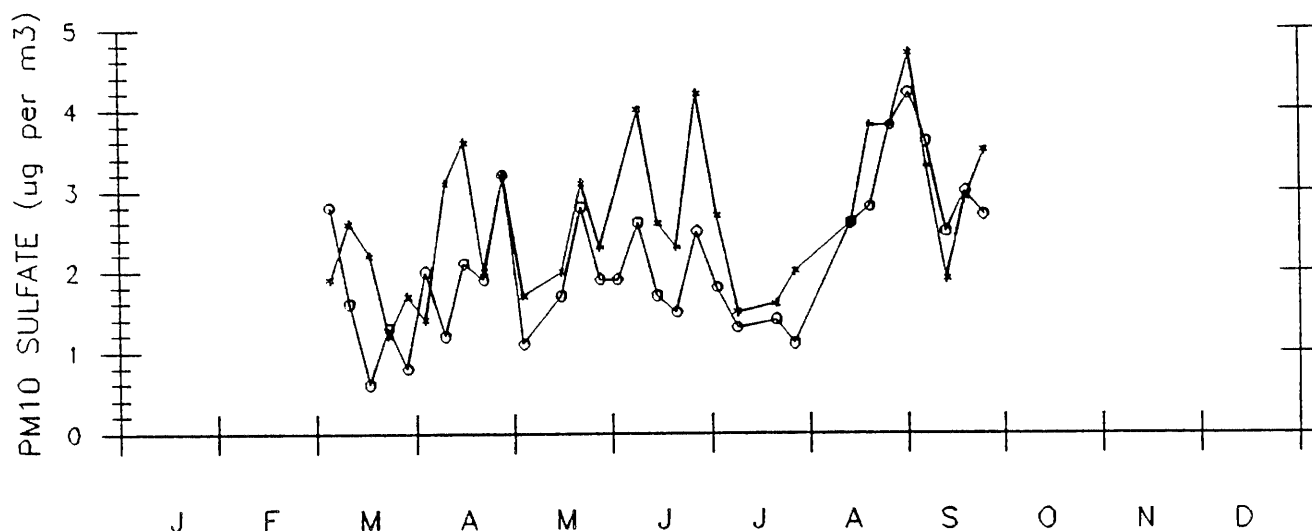


Figure 12: Sulfate in San Joaquin Valley, 1987

Unfortunately, data on particulate size and trace elemental composition are more difficult to find. The most extensive sets of size-resolved compositional data in the San Joaquin Valley were taken in the early 1970s for the California Air Resources Board. Tables 2 and 3 (Cahill et al. 1976) summarize them.

These data are variously revealing. First, coarse soils play a major role in summer PM10 values in the Central Valley, but their ability to travel into the western Sierra slope is limited. Second, while many major components north (Sacramento) and south (Bakersfield) are comparable to Sequoia National Park, some trace elements are sharply different. Specifically, nickel levels in the Bakersfield area are much higher than at other sites because of the local combustion of heavy oil. While efforts have been made to reduce this type of emission in the past 10 years, the presence of nickel is still a potential tracer of the Bakersfield area. Third, lead levels have fallen precipitously since 1977.

Table 2: Sacramento's elemental size distributions 1973-1974

SACRAMENTO		July, August, September, 1973		January, February, March, 1974	
Major Elements, (sets corr. >0.8)		Ratios	Mass (ng/m ³)	Percent in Stage St. 3 St. 2 St. 1	Percent in Stage St. 3 St. 2 St. 1
Aluminum	0.26				
Silicon	1.00				
Potassium	0.18				
Calcium	0.16				
Titanium	0.027				
Manganese	0.015				
Iron	0.36				
Soil set			6,700	20% 20% 60%	14% 37% 49%
with oxides (appr.)			13,400		
Sodium			620	23% 68% 9%	13% 52% 35%
Magnesium			130	35% 42% 23%	7% 48% 45%
Sulfur			1,020	76% 23% 1%	62% 35% 3%
S as SO ₄			3,060		
Chlorine			340	<1% 30% 70%	N.D. N.D. N.D.
Vanadium			6	N.D. N.D. N.D.	
Chromium			1	N.D. N.D. N.D.	
Nickel			<0.3		
Copper			8	69% 21% <1%	72% 21% 7%
Zinc			30	58% 28% 14%	60% 32% 8%
Bromine	0.22				
Lead	1.00				
Auto set			860	86% 11% 3%	80% 18% 2%

Table 3: Bakersfield's elemental size distributions 1973-1974

ELEMENTAL SIZE DISTRIBUTIONS						
BAKERSFIELD						
July, August, September, 1973			January, February, March, 1974			
Major Elements, (sets corr. >0.8)	Ratios	Mass (ng/m ³)	Percent in Stage St. 3 St. 2 St. 1	Ratios	Mass (ng/m ³)	Percent in Stage St. 3 St. 2 St. 1
Aluminum	0.31			0.23		
Silicon	1.00			1.00		
Potassium	0.23			0.21		
Calcium	0.27			0.32		
Titanium	0.032			0.025		
Manganese	0.006			0.005		
Iron	0.40			0.39		
Soil set		10,300	14%	12%	4,980	16%
with oxides (appr.)		20,600		73%	10,000	27%
Sodium		170	15%	84%	210	5%
Magnesium		75	16%	84%	60	36%
Sulfur		1,500	83%	16%	1,900	<5%
S as SO ₄		4,500		0.7%	5,700	17%
Chlorine		18	2%	9%	240	37%
Vandium		19	27%	8%	18	<5%
Chromium		0.7	N.D.	N.D.	0.7	N.D.
Nickel		22	96%	4%	42	76%
Copper		14	49%	29%	26	24%
Zinc		47	36%	34%	66	39%
Bromine	0.24					56%
Lead	1.00					36%
Auto set		1,320	88%	10%	1,450	74%
			2%			24%
						2%

Additional detail on Central Valley aerosols by size and composition is available from a sampling site at Davis. While the DRUM sampler was being tested, extensive tests were done at Davis in summer 1984. These data, while separated geographically from the potential source areas, do provide information on the particulate size profiles of three major components of the summer aerosols: soils, sulfates, and smoke. Figure 13 gives results for these tests (Cahill et al. 1986; Raabe et al. 1988).

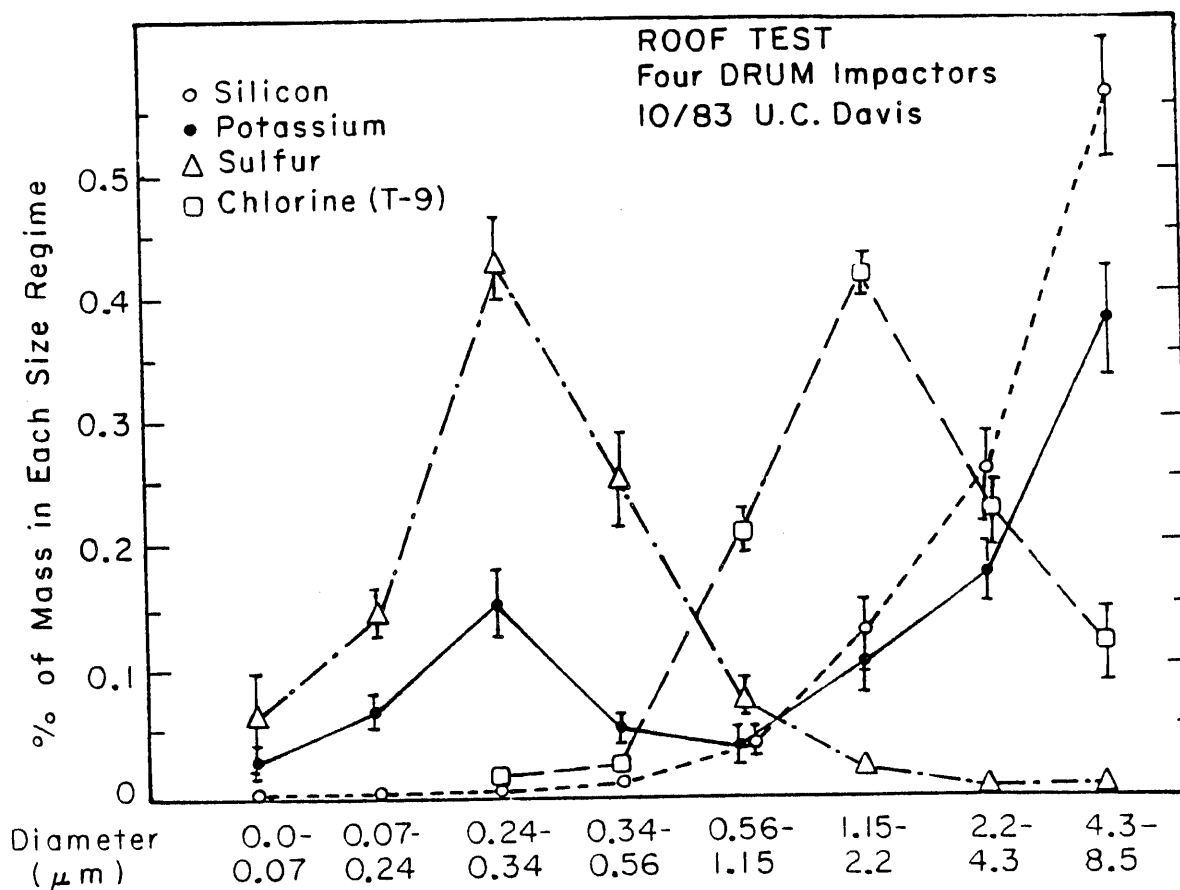


Figure 13: Particulate size distribution of Central Valley aerosols, Davis, summer 1984

A number of points should be noted. Aerosols coming from soils are very coarse (Al, Si, Ca, Ti, Fe) and may not transport efficiently in moderate winds. Potassium possesses both a soil component (coarse) and a smoke component ($D_p \approx 0.3 \mu\text{m}$). Sulfates are purely accumulation mode aerosols, $D_p \approx 0.3 \mu\text{m}$, and thus capable of efficient transport. Finally, the chlorine from sea-salt, which starts out at the coast resembling soils in their coarseness (Cahill et al. 1976), peaks at $D_p \approx 0.3 \mu\text{m}$ after traveling the 60-100 km (37-62 miles) to Davis on the strong (wind velocity ≥ 10 m/sec) summer "bay breeze." A similar effect will appear later when we examine soil profiles at Sequoia.

California's Central Valley possesses strong local and regional sources of particulate matter which are likely to be transported into the acid deposition test sites. However, the dominant summer mass component, coarse soils, should not transport as efficiently as the accumulation mode aerosols: sulfates, smoke, and (presumably) nitrates and non-smoke organic matter.

Characteristics of mountain aerosols--regional

The terrain and meteorology of the western slope of the Sierra Nevada mountains maintain a high degree of consistency everywhere, from just north of the Tehachapi Mountains, near Bakersfield, to the north end of the Sacramento Valley, near Red Bluff. Thus it is reasonable to examine how well the air quality data from Sequoia represent this entire slope, because the results at Sequoia can be extended to a much wider and biologically important area of California. Since data exist through the work of the National Park Service and Environmental Protection Agency (Cahill et al. 1985), we can compare these sites for concentrations of fine ($<2.5 \mu\text{m}$) sulfur aerosols, which are almost totally anthropogenic in origin at sites shown in Figure 1.

Summer data for the period 1982-1985 appear below (Table 4). The Giant Forest (Lower Kaweah) site at Sequoia can be directly compared to existing National Park Service sites in the western United States, especially those sites with similar vegetation and elevation. Such sites include Crater Lake, Lassen, and Yosemite national parks and Lava Beds National Monument. Death Valley and Joshua Tree national monuments are included as comparisons. Sulfur is used as a comparison element since it is a major component in fine particulate mass and a significant factor in acidity. The sulfur is largely generated by human activities.

Sequoia does not appear dramatically different from other California sites from Yosemite southward. These sites show, however, about 2 1/2 times the sulfur of the three northern park sites, which are among the cleanest in the United States. Notably, sulfur levels at Sequoia are only about 20% of those in the eastern United States (Cahill et al. 1985).

Table 4: Mean summer sulfur concentrations at NPS sites (1982-1985)

	Elevation (meters) (feet)		Sulfur Concentration (ng/m^3)	Equivalent $\text{SO}_4^{=}$ ($\mu\text{g}/\text{m}^3$)
Crater Lake NP	1982	6500	194	0.58
Lava Beds NM	1464	4800	191	0.57
Lassen NP	1800	5900	221	0.66
Sacramento	-----			
Yosemite NP	1616*	5300*	454	1.36
Sequoia NP	1952	6400	535	1.61
Bakersfield	-----			
Death Valley NM	122	400	496	1.49
Joshua Tree NM	1403	4600	563	1.70

* Ridge site

(NP - National Park; NM - National Monument)

Not only are the mean values of sulfur similar at Yosemite and Sequoia; sulfur values at these sites correlate reasonably well. Figure 14 shows the results for summer 1985 at these sites, with a correlation coefficient of 0.6 in response to synoptic meteorology.

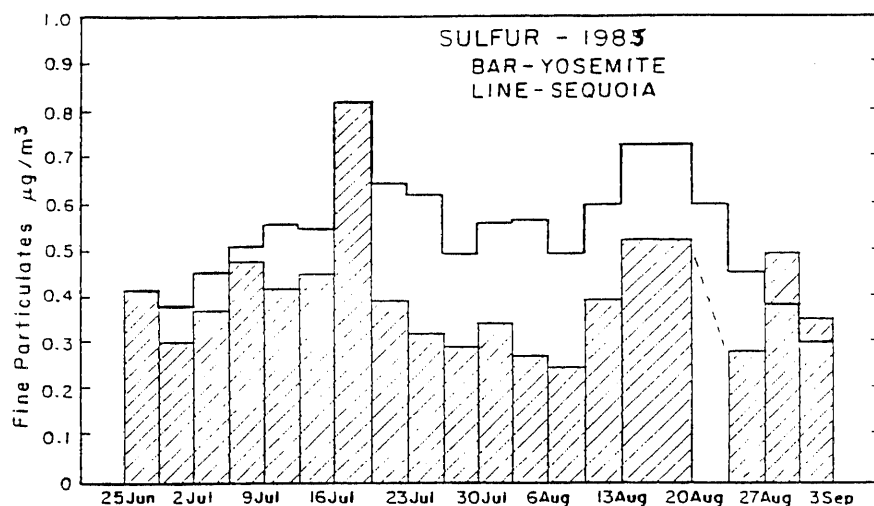


Figure 14: Comparison of sulfur aerosols, Sequoia vs Yosemite, near 6000-ft elevation, 1985

A comparison of fine and coarse mass and its components (Table 5) yielded further insight into the nature and sources of particulate matter at Sequoia (and potentially other sites around 2000 m [6560 ft] elevation on the western Sierra slope). A consistent picture emerges. Particulate matter at Sequoia is 34% higher than at Yosemite's ridge site, chosen to avoid local pollution levels in Yosemite Valley. Sulfates are 40% higher at Sequoia, but nickel is 320% higher. Since nickel is a major tracer of fuel oil combustion, and since nickel levels in the Bakersfield area are much higher than in the Sacramento area, we conclude that Sequoia undergoes greater influence from the southern San Joaquin Valley than does Yosemite.

TABLE 5: Particulate matter at California National Parks (all values $\mu\text{g}/\text{m}^3$), except those in parentheses, which are ng/m^3)
June, July, August, 1985

	SEQUOIA	YOSEMITE	RATIO (Sequoia/Yosemite)
MASS			
Coarse	12	8.9	1.35
Fine	13	9.7	1.34
TOTAL	25	18.6	1.34
FINE COMPONENTS			
SOILS(*)	1.2	1.0	1.20
SULFATE(**)	2.4	1.7	1.4
Sulfur	(576)	(418)	1.4
V	(1)	(<1)	>1
Ni	(2.1)	(0.5)	4.2
SMOKE	3.4	2.3	1.5
K	(169)	(116)	1.5
AUTOMOTIVE			
Pb	(10)	(4)	2.5
Br	(4.6)	(2)	2.3
SALTS			
Na	(119)	(89)	1.3
Cl	(2)	(<2)	>1
MISC. METALS			
Cu	(1)	(4.1)	0.24
Zn	(5)	(5.0)	1.00

* Al, Si, Ca, Ti, Fe + oxides

** assumes $(\text{NH}_4)_2\text{SO}_4$, (H/S 8:1)

In order to examine these relationships, we examined the particulate matter at Sequoia and Yosemite much more extensively in 1986 and 1987. Sampling protocols were modified to allow 24-hour sample durations at both sites, and sampling was extended to all seasons. Data from both sites were analyzed under the National Park Service Quality Assurance Protocols.

Figure 15 compares the fine sulfur ($D_p < 2.5 \mu m$) at both sites for 1987. Several points deserve comment. First, mean summer levels of sulfur are higher at Sequoia (Giant Forest site) than at Yosemite, but now the ratio is 1.8 times greater at Sequoia. This ratio, somewhat larger than the 1.4 ratio seen in 1985, may reflect to some degree a relocation of the Yosemite site in 1986 to Turtleback Dome, with a gain in elevation from 1616 m (5300 ft) in 1985 to 1891 m (6200 ft) in 1987.

FINE SULFUR — 1987

BAR = Yosemite LINE = Sequoia

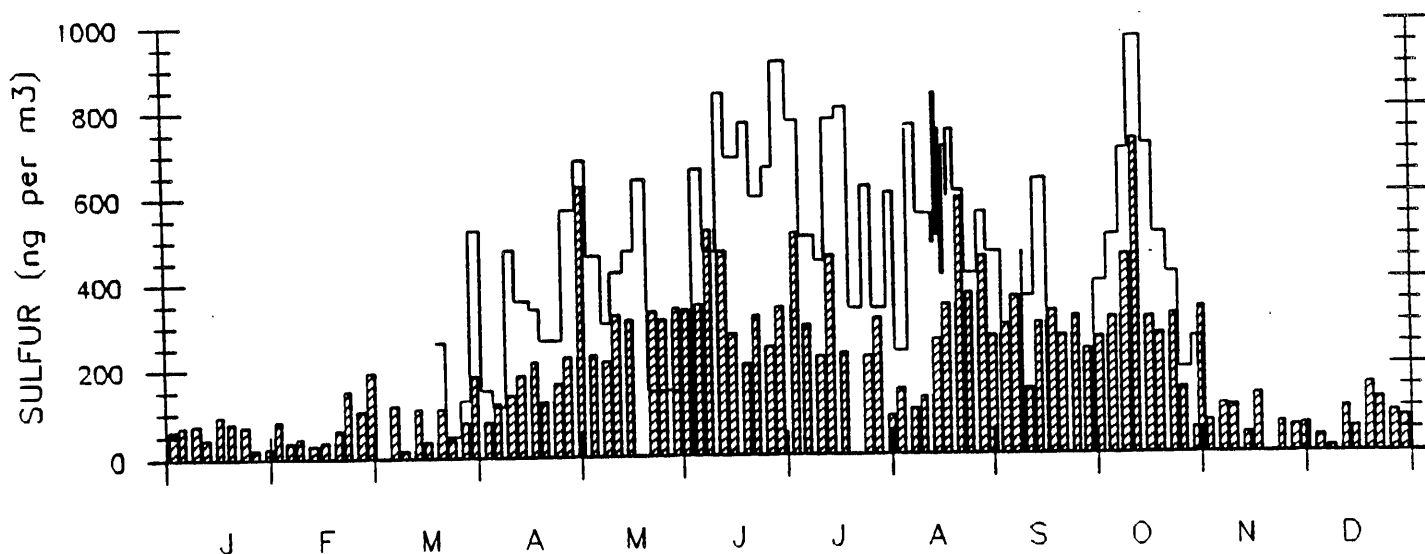


Figure 15: Comparison of sulfur aerosols, Sequoia vs Yosemite, near 6000 ft elevation, 1987

Also noteworthy is the abrupt rise of sulfur values at both Sequoia and Yosemite in March and April and the precipitous fall around November 1. These changes are opposite to those on the floor of the Central Valley, which achieves its highest sulfate levels in the winter (ARB Monitoring Data). We interpret this as the decoupling of the mountain sites from the Central Valley when the characteristic and strong inversion sets in, at the valley floor. This abrupt decrease in aerosol levels will clearly have a direct impact on dry deposition rates during fall, winter, and spring months in the mountains.

The concentration levels generally follow the same pattern of fluctuation at both sites, particularly for silicon, and most major peaks occur simultaneously (see Figure 16).

FINE SILICON — 1987

BAR = Yosemite UNE = Sequoia

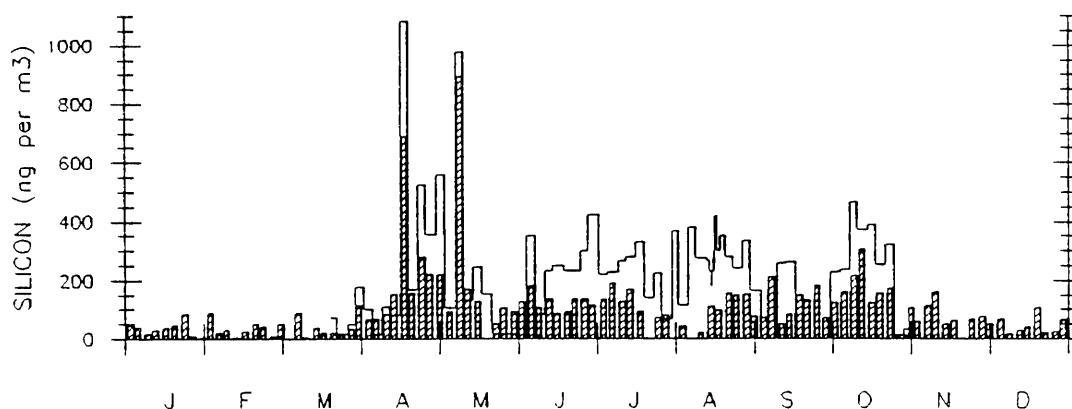


Figure 16: Comparison of silicon aerosols, Sequoia vs Yosemite, near 6000 ft elevation, 1987

A statistical analysis of the same data, shown in Table 6, reveals good correlation for some elements such as the soil related ones (Si, Fe, Al). A lower, but significant, degree of correlation occurs for potassium, sulfur, and sodium. The values of R listed are very close to those calculated for PM10 data from Modesto and Visalia, the two nearest ARB sites in the San Joaquin Valley, which are as far apart as Sequoia and Yosemite. Note also the valley sulfate level at Visalia is only about 80% higher than that at the Giant Forest site, Sequoia. (Recall figures 11 and 12.)

Table 6: Correlation analysis of summer 1987 aerosol data

Element	R-squared	Average Ratio (Sequoia/Yosemite)
S	0.360	1.810
Si	0.699	1.850
Fe	0.608	1.340
Al	0.636	1.450
K	0.387	1.410
Pb	0.018	3.390
Zn	0.009	1.640
VISALIA/MODESTO		
SO ₄ --	0.350	
PM10	0.630	

Not all the elements at the two sites correlate. The data for lead and zinc, the two most prominent heavy metals detected, show no relationship. (See Figure 17.)

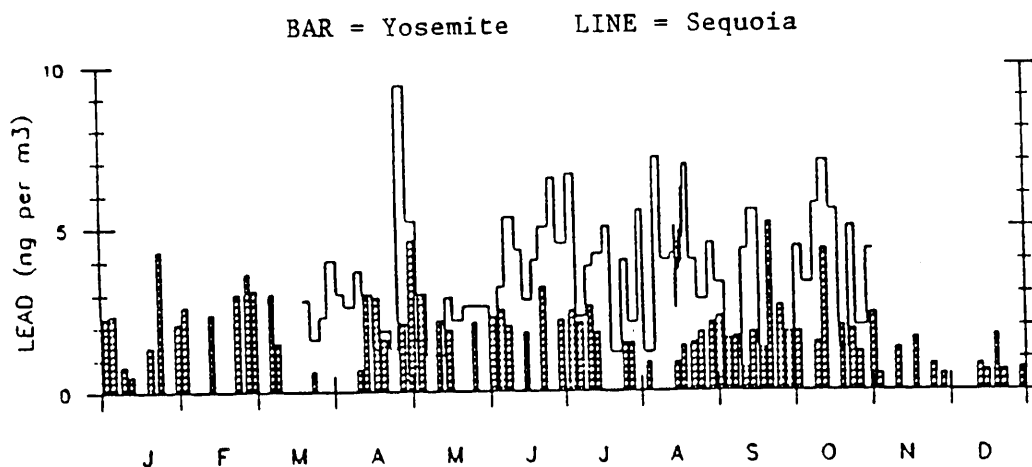


Figure 17: Comparison of lead aerosols, Sequoia vs Yosemite, near 6000 ft elevation, 1985

This lack of relationship can be attributed to the proximity of the source to the site. While lead and zinc are generally attributed to local sources (i.e., automobile exhaust), the other elements are all related to more distant sources, except potassium, which may be from both local and distant sources. Most sulfur results exclusively from oil or coal-fired electric power generation, for which no stations exist near either site. Sodium is typically brought in by marine air masses, but is also a soil component. The three soil elements which show the highest correlation would be assumed to be potentially local in origin, in most cases. However, the two park sites both sit on exposed granitic bedrock above heavily forested slopes, so very little local dust occurs. The potential sources of potassium (see Figure 18), observed in smoke from burning wood or other vegetation, are local campfires, agricultural burning and brush fires in the valley and foothills, and forest fires anywhere in the region. Considering this variety of sources, the correlation between the two sites is surprisingly good.

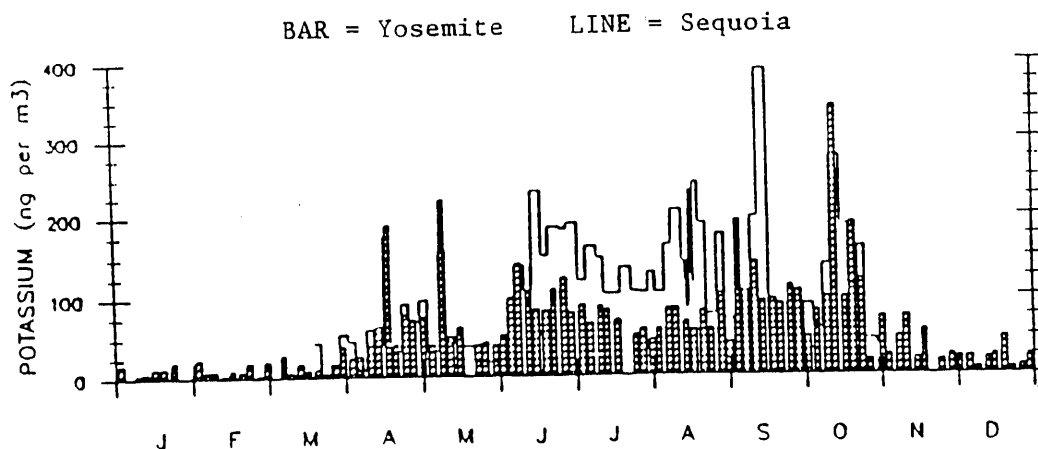


Figure 18: Comparison of potassium aerosols, Sequoia vs Yosemite, near 6000 ft elevation, 1985

Another distinction between sources may explain the higher correlation of soil elements relative to sulfur, sodium, and potassium. The presence of high levels of crustal dust at remote sites results primarily from meteorology at lower elevations in the region, namely dry windy conditions in the valleys and deserts. Because of the meridional geography of the region, the entire slope of the Sierra might be subject to dust transported from the San Joaquin valley. Sulfur and potassium (smoke), conversely, originate from sources often located much nearer to one site than the other. Depending on wind direction and stability, material from a source may reach one site more frequently than the other site. For sodium, the presence of the Coast Range (which blocks marine air from directly reaching the Sierra via westerly winds) restricts flow so that the marine influx is essentially from the northern end of the San Joaquin Valley.

Figure 19 shows the concentration of fine nickel aerosols at Sequoia and Yosemite. There is no significant correlation between the two sites, and Sequoia continues to show high nickel values during infrequent episodes.

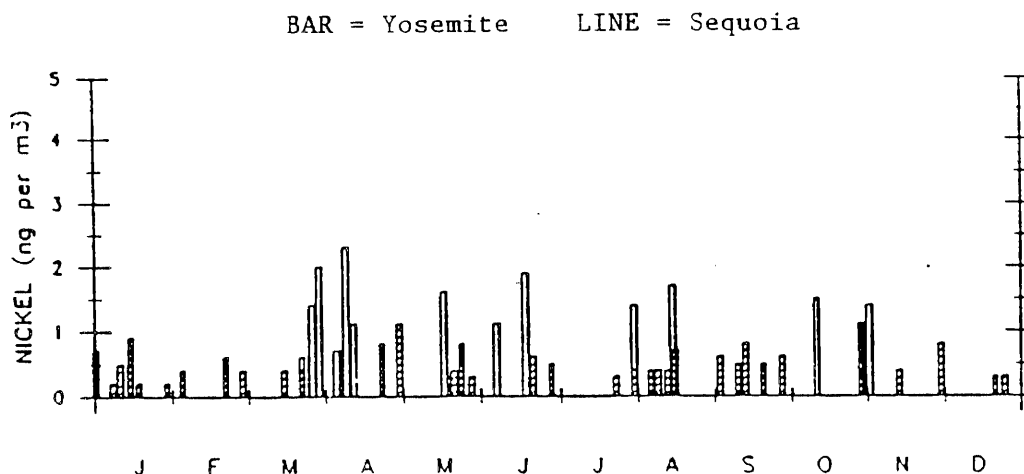


Figure 19: Comparison of nickel aerosols, Sequoia vs Yosemite, near 6000 ft elevation, 1985

Comparative analysis of data from the two sites supports the following conclusions:

- (1) Both Sequoia and Yosemite are representative of high altitude conditions throughout the western slope of the Sierra Nevada.
- (2) Data from Yosemite, recorded year round by IMPROVE, can be used to estimate trends in air quality at Sequoia and other locations where no local data are available.
- (3) Pollution in the high Sierra Nevada is affected by distant regional sources and likely to be dependent on mesoscale or synoptic meteorologic conditions.
- (4) Air quality at Sequoia is generally poorer than at Yosemite.
- (5) The level of nickel at Sequoia is two to three times that at Yosemite, confirming the 1985 data (Figure 19). From the Central Valley data, the major nickel source is near Bakersfield.

In spring 1988, the Yosemite site was converted to the IMPROVE (Interagency Monitoring of Protected Visual Environments) protocol of the NPS, EPA, Forest Service, BLM, and Fish & Wildlife Service. This provides a continuing record of Wednesday and Saturday 24-hour samples and greatly extended mass, elemental, and chemical analyses (Eldred et al. 1988). Thus, because of the similarities between the Yosemite and Sequoia sites, data will continue to be available potentially relevant to regional aerosol patterns on the western slope of the Sierra Nevada range (Figure 20).

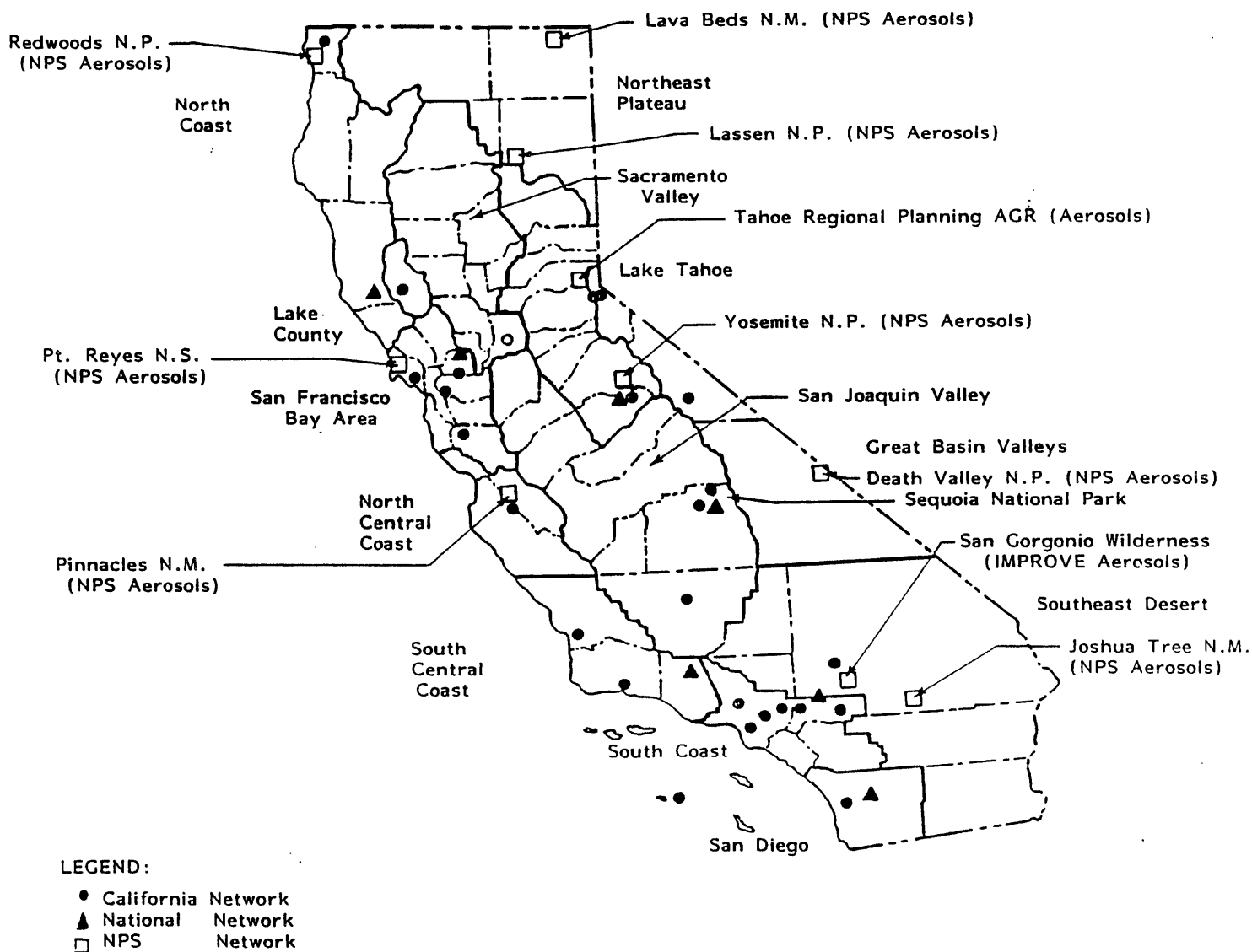


Figure 20: California deposition and remote aerosol sites

Characteristics of mountain aerosols--local

One of our most important tasks was to evaluate the transport of Central Valley aerosols into the biologically sensitive forest environment around and above 2000 m (6560 ft) elevation. Such transport depends on the local meteorology, dominated in the summer by the regular terrain wind. Two methods used to evaluate the nature and source of the mountain aerosols were monitoring weekly average values at closely located sites varying in altitude, and examining aerosols with high size and time resolution at the key site, Giant Forest.

Profiles versus elevation

The topography of the three key sites in Sequoia appears in Figure 21. While the Ash Mountain, Giant Forest (Lower Kaweah), and Emerald Lake sites are separated laterally by only a few miles (as the crow flies), they are separated by dramatic differences in elevation [564 m (1850 ft)]. The Ash mountain site, at 560 m (1837 ft), lies consistently below the top of the characteristic well-mixed surface boundary layer of the San Joaquin Valley in summer. The Giant Forest site, at Lower Kaweah just west of the main visitor area, is situated on the very edge of a sharp decline at an elevation of 1940 m (6400 ft). The Emerald Lake site was originally situated on a ridge at 3040 m (10000 ft) in 1985, but then re-located in 1987 to a point near the lake 80 m (270 ft) lower.

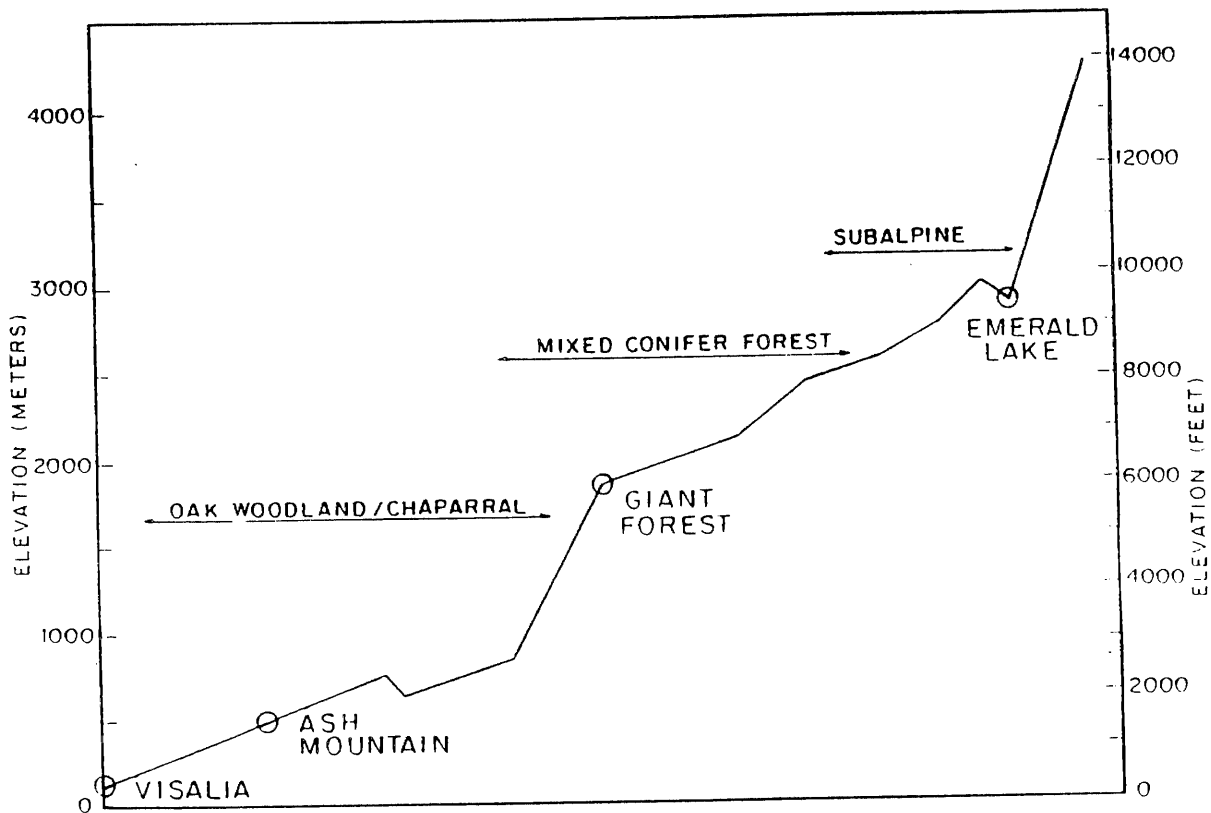


Figure 21: Schematic topography of sampling sites, Sequoia NP

Figure 24 shows the effect of elevation on the concentration of fine mode sulfur aerosols during summer 1985 (the only year for which such data are available).

Ash Mountain values are higher than Giant Forest values by about 20%, and the two sites clearly are highly correlated by time (corr. coeff. = 0.72). Emerald Lake values are sharply lower, 44% of the Giant Forest values, and the high correlation in time evident in June and July (corr. coeff. = 0.78) has weakened by August to 0.53. Thus, while Ash Mountain and Giant Forest are closely coupled despite a 1380 m (4528 ft) difference in elevation, Giant Forest and Emerald Lake are partially decoupled despite close proximity in distance and only an 870 m (2854 ft) difference in elevation. It is remarkable that Yosemite, over 144 km (90 miles) distant, is better correlated with Sequoia's Giant Forest site than Giant Forest is with the Emerald Lake site. The key role of elevation on particulate concentrations is clear. The lack of temporal correlation between the Giant Forest and Emerald Lake sites raises the possibility that some of the sulfur at Emerald Lake may be from a different source than that at Giant Forest.

Examining the mass and elemental record (Table 7) reveals certain trends in the data at the three elevations.

Table 7: Aerosol mass and components vs elevation

	Ash Mountain	Sequoia Giant Forest	Emerald Lake	Ratio EL/GF
Al	127.0 ng/m ³	109.0	35.0	0.32
Si	346.0 ng/m ³	253.0	121.0	0.48
S	676.0 ng/m ³	535.0	250.0	0.47
Cl	0.0 ng/m ³	0.0	0.9	----
K	142.0 ng/m ³	147.0	49.0	0.33
Ca	50.0 ng/m ³	35.0	17.0	0.49
Ti	7.0 ng/m ³	3.7	2.6	0.70
V	1.4 ng/m ³	1.1	0.4	0.36
Cr	-----	-----	-----	-----
Mn	1.7 ng/m ³	1.6	0.9	0.56
Fe	98.5 ng/m ³	62.1	32.0	0.52
Ni	3.5 ng/m ³	2.6	2.4	0.92
Cu	2.7 ng/m ³	1.0	0.9	0.90
Zn	5.8 ng/m ³	4.5	1.6	0.36
Br	5.0 ng/m ³	5.3	2.0	0.38
Pb	14.0 ng/m ³	9.9	4.2	0.42
Soot C	380.0 ng/m ³	360.0	109.0	0.30
Mass (Fine)	10.67 µg/m ³	12.45	5.3	0.43
Mass (Coarse)	21.56 µg/m ³	12.29	N/A	N/A
Mass (Total)	32.23 µg/m ³	24.74	N/A	N/A
S/ Fine Mass	6.3%	4.3%	4.7%	
(NH ₄) ₂ SO ₄ / Fine Mass	26.1%	18.2%	19.8%	

First, coarse mass falls off sharply from Ash Mountain to Giant Forest (Ratio=0.57), but fine mass actually increases (Ratio=1.17). All major elemental species, however, fall off in a rather consistent fashion (Ratio=0.77 to 1.18, including soot). Since these include species from very different sources (soils, smoke, anthropogenic sulfur, automotive fuel, oil, and others), this consistency indicates that what we are seeing at the Giant Forest site is a well-mixed Central Valley aerosol, merely reduced by about a quarter during transport. Clearly, the coarse particles are more strongly attenuated than fine particles, as will be confirmed in the next section. Noteworthy also is that the Ash Mountain sulfur values, when converted to sulfate ($\times 3.0$), resemble typical sulfate levels at Visalia (Figure 12). The additional fine mass must consist of elements too light to give X-rays, most likely organic matter and nitrates.

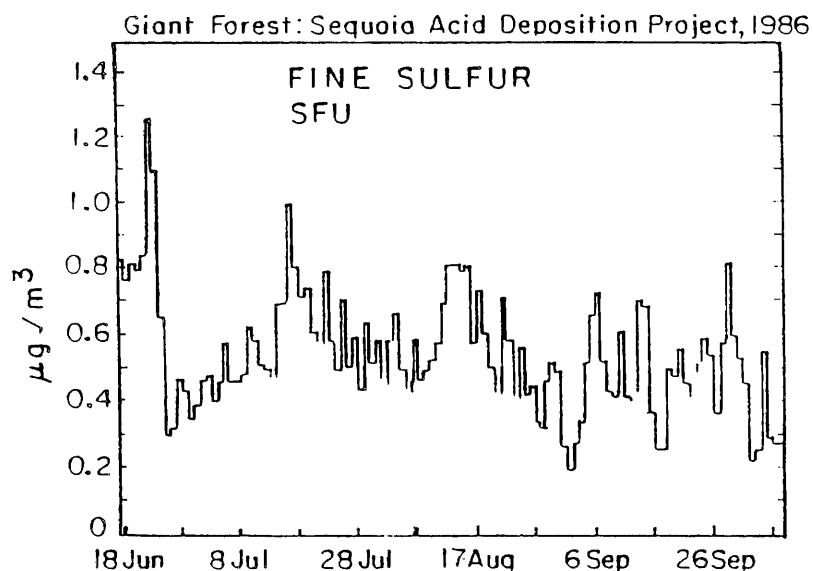


Figure 22: Fine particulate sulfur, Giant Forest, 1986

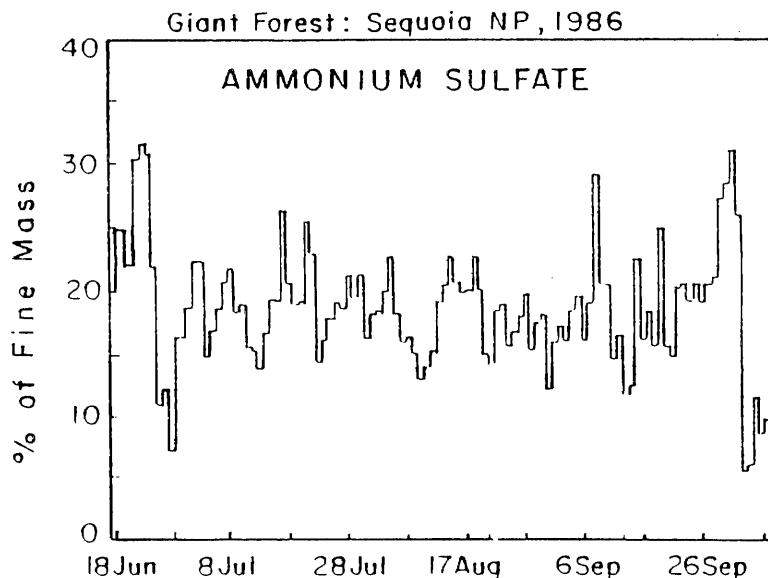


Figure 23: Fine particulate ammonium sulfate (inferred from sulfur) as a percent of fine mass, Giant Forest, 1986

This hypothesis is supported (but not proven) by the relatively high hydrogen values seen at Giant Forest and their lack of correlation with sulfur. This has proven to be a good signature of organic matter (Cahill et al. 1986b; Cahill et al. 1986c). Unfortunately, no similar data are available for the Ash Mountain site, but, pertinently, the fall off of nickel from Ash Mountain to Giant Forest (Ratio=0.74) closely matched all other fine particles.

Moving from Giant Forest [1940 m (6365 ft)] to Emerald Lake [2819 m (9249 ft)], the picture changes dramatically (Figure 24).

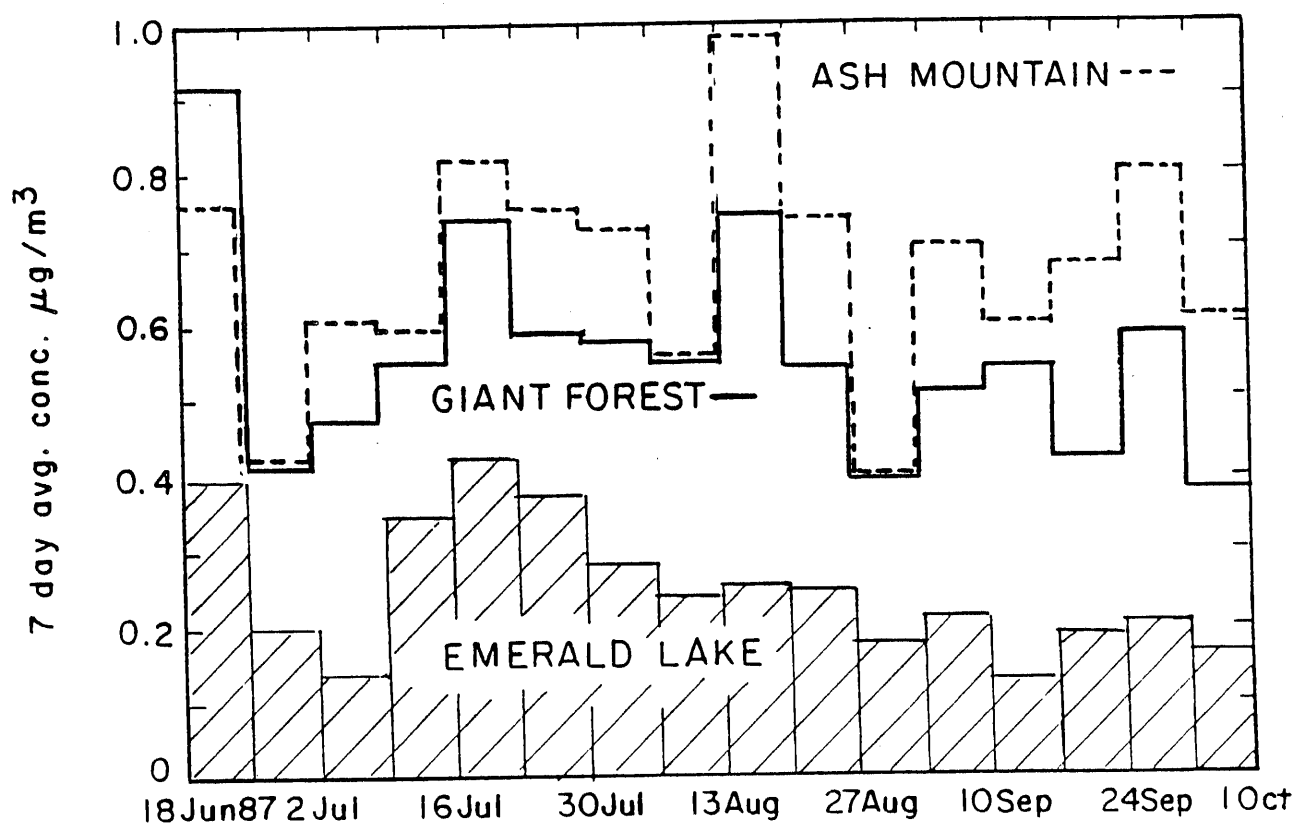


Figure 24: Sulfur aerosols vs elevation, Sequoia NP, 1985

Just as the temporal correlation falls off abruptly, the mass and elemental components also fall off, but not in the uniform manner shown going from Ash Mountain to Giant Forest. The ratios appear in Table 6. The fine mass falls off sharply (Ratio=0.43), as do soils (Ratio=0.51/0.12), sulfur (Ratio=0.47), and automotive and urban aerosols (Ratio=0.39/0.03). While vanadium falls into the same pattern (Ratio=0.36), nickel and copper hardly fall off at all (Ratios=0.92;0.90, respectively). Recalling the high sulfur, high nickel aerosols of the Bakersfield area, we hypothesize that the lack of sulfur correlation between Emerald Lake and Giant Forest, as well as the elevated tracer levels, points to an admixture of sulfur at high elevations that does not come from the well-mixed Central Valley aerosol at Ash Mountain but from sources further south.

Further support comes from meteorology for the hypothesis that some of the sulfur (presumably sulfate) at Emerald Lake comes from the Bakersfield/ California Desert/ Arizona area. A remnant of a tropical hurricane was present on August 17 (Ewell et al. 1988), resulting in thunderstorms along the eastern Sierras. During the week of August 20, nickel reached the highest level recorded at Emerald Lake (16.9 ng/m^3), higher than the similar but lower peak seen in the 24-hour sample of Giant Forest on August 20 (6.9 ng/m^3), and much higher than the 7-day average at Giant Forest (4.6 ng/m^3).

Thus the aerosols present at Emerald Lake differ quantitatively and qualitatively from those present at Ash Mountain and Giant Forest, indicating different transport mechanisms and probably resulting in different deposition phenomena.

Profiles versus size and time

To proceed further in time resolution means to become involved in the details of the strong diurnal patterns. This requires time-resolution of better than 6 hours, which is possible for the Davis Rotating-drum Unit for Monitoring (DRUM). This inertial impactor was modified and calibrated in 1987 (Raabe et al., 1988) to deliver 9 size ranges between $0.07 \mu\text{m}$ and $13 \mu\text{m}$. The data were also improved by a new elemental analysis system with two X-ray detectors, delivering sharply lower detection limits for trace elements.

Data were taken during what appeared to be a typical period, September 1987, at a time when the Emerald Lake ozone monitor was working well. Examples of the data record appear in Figures 25 and 26.

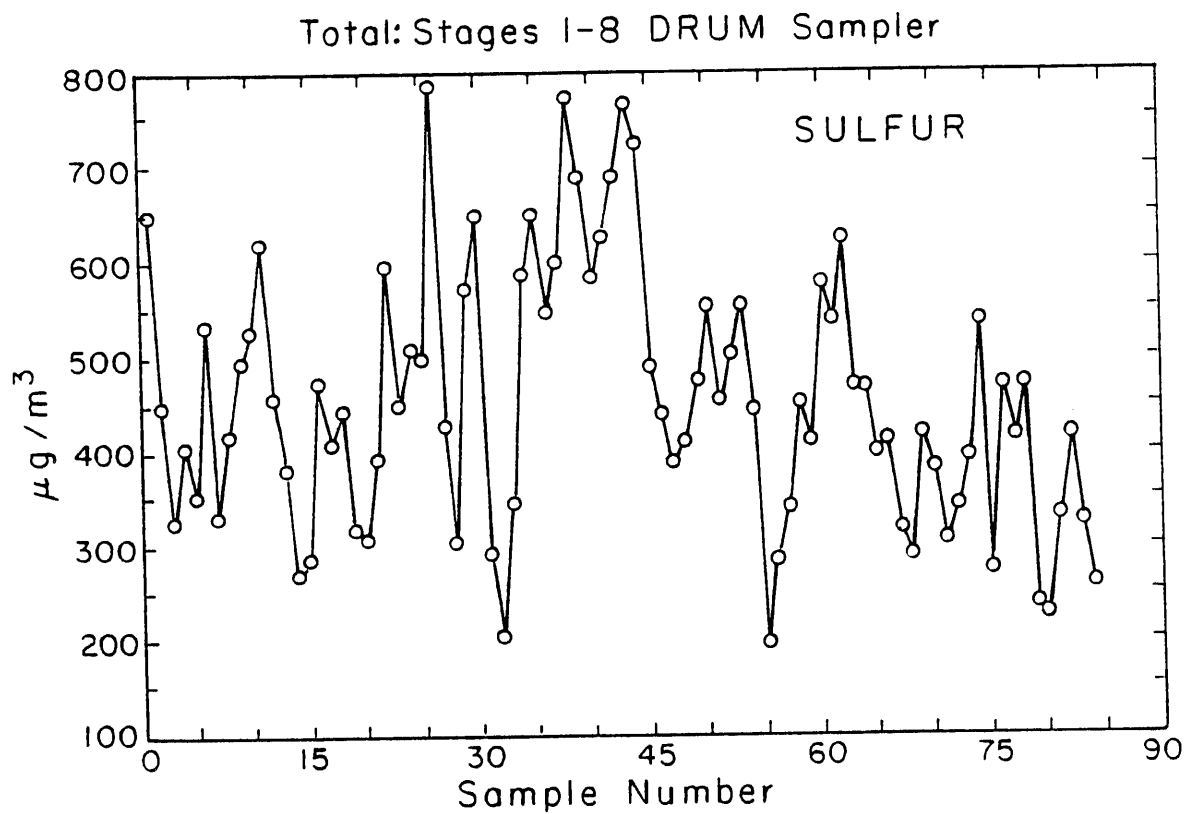


Figure 25: Total sulfur at Giant Forest (September 1-20, 1987)

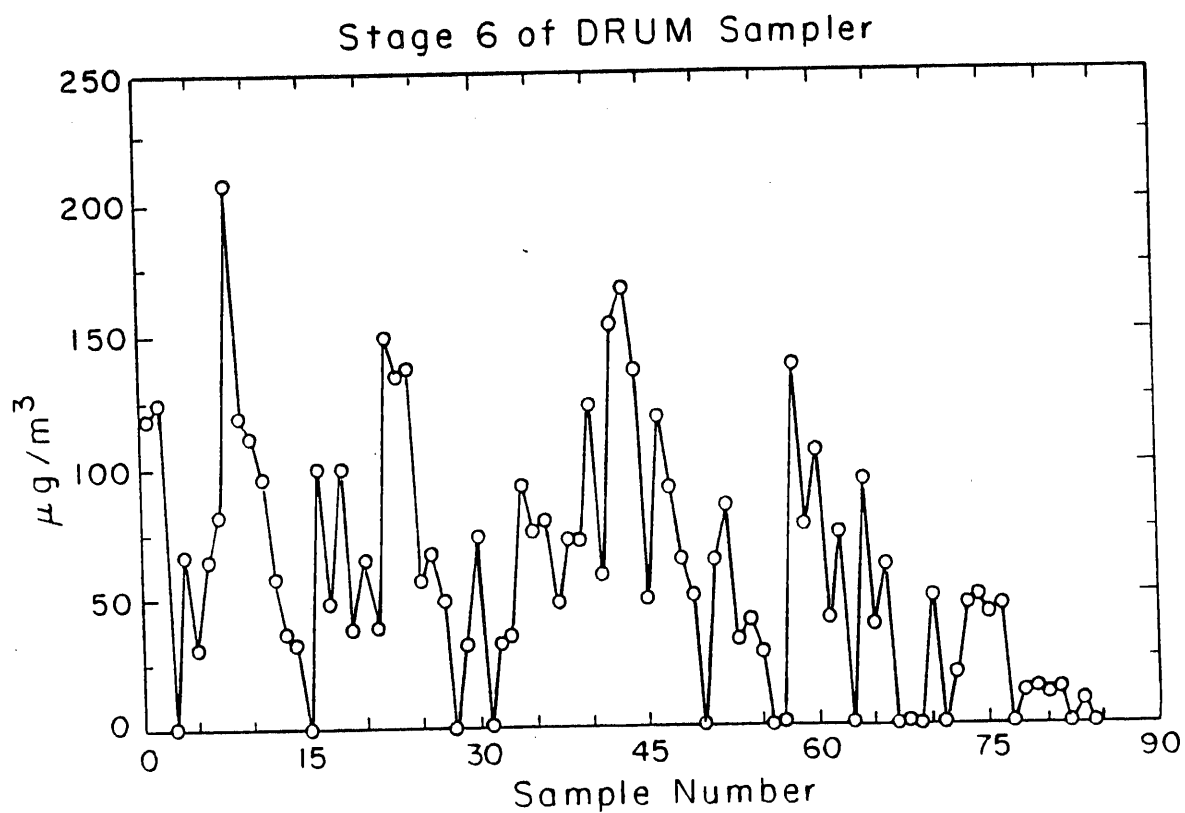


Figure 26: Accumulation-mode potassium at Giant Forest (September 1-20, 1987)

The addition of the diurnal pattern to the synoptic variations gives a total pattern that is difficult to interpret. Since the synoptic patterns are already available from the filter data, we can reduce the data to emphasize the diurnal pattern. The data are presented below in a way that illustrates both the size distribution, important for dry deposition studies, and the time distribution, important for source attribution.

Figure 27 shows the size and time distribution for the characteristic soil elements silicon, calcium, and iron.

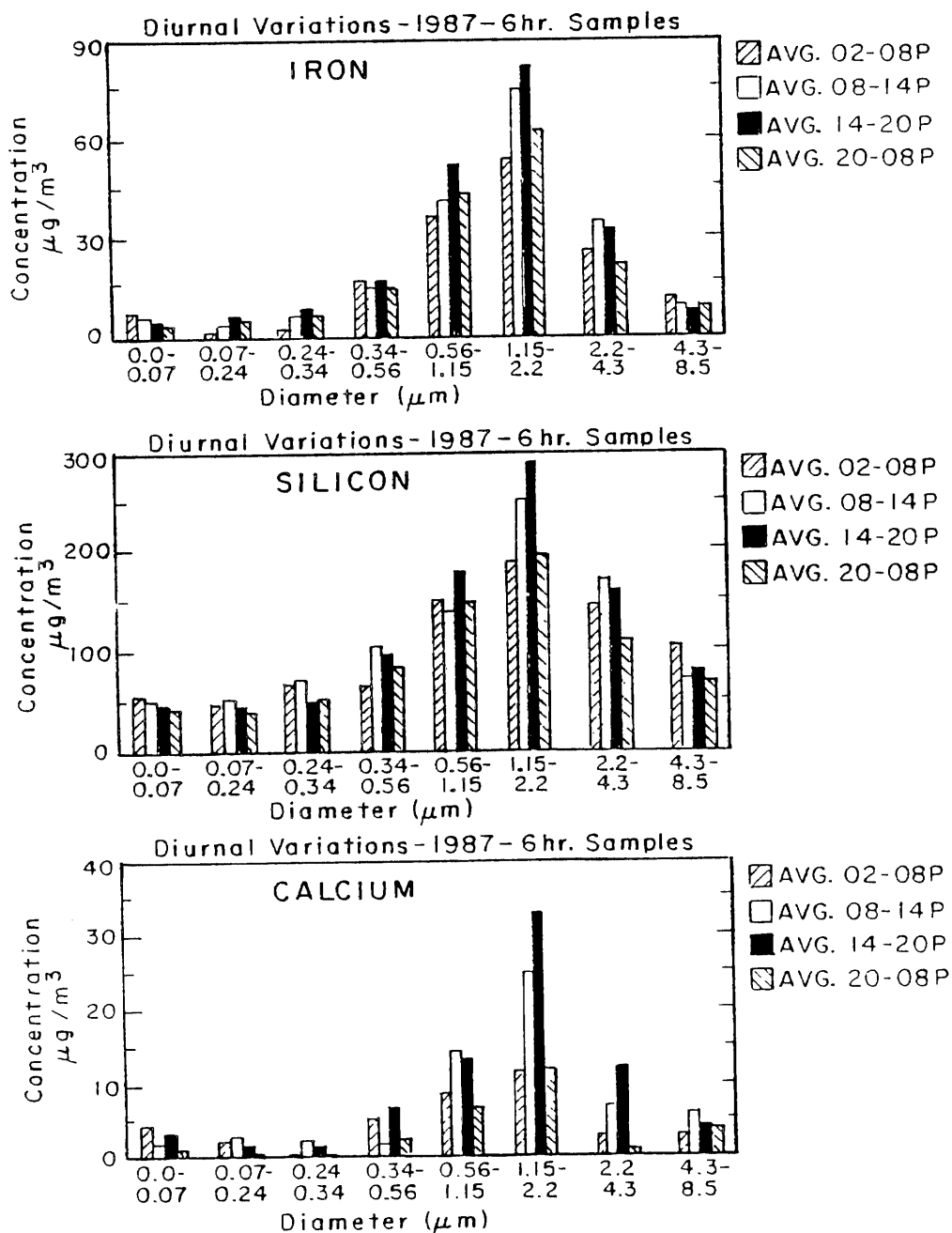


Figure 27: Soil derived particles, Giant Forest, 1987

These results should be compared with the soil elements shown earlier (Figure 13) at Davis. The peak in the distribution is no longer in Stage 1 (13 to 8.5 μm) but in Stage 3 (4.2 to 2.1 μm), normally the minimum in the bi-modal distribution. Thus, either the local soils generate anomalous size distribution in aerosols, or the soil aerosols are dominated by transported aerosols from the San Joaquin Valley and, in transport, they have lost their coarsest particles.

Support for the second hypothesis comes from the typical behavior of local Giant Forest soils, the relative lack of exposed soil areas upwind of the sampling site (daytime), and the similar behavior seen at Davis in transported sea salt aerosols, which also lose their coarsest particles in qualitative agreement with transport theory. The strong implications of this result for dry deposition include a lower settling velocity for the soil fraction that might typically be expected.

Noteworthy also is the enhancement of soils occurring during daytime upslope winds that favor transport from the San Joaquin Valley. This phenomenon is most pronounced for calcium and leads to the surprising conclusion that the downslope soil aerosols are slightly different chemically from the upslope soil aerosols. A diversity of sources is suggested.

Figure 28 shows similar plots for sulfur and potassium. Here the size distributions are very different, peaking in the 0.34 to 0.56 μm for sulfur and potassium.

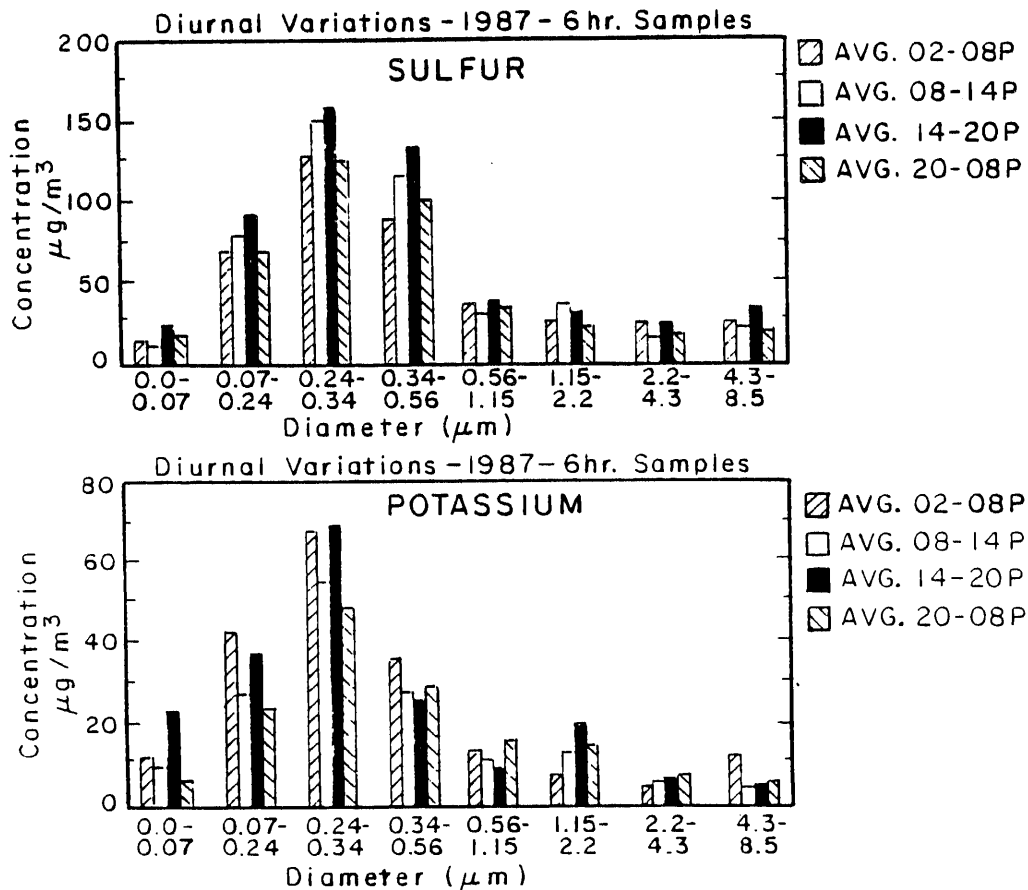


Figure 28: Sulfur and potassium, Giant Forest, 1987

Sulfur is the most important of these species, associated with acidic aerosols and deposition, and possibly serving as a surrogate for nitrogen. (Matsuda et al., 1985; Cahill et al., 1989). It peaks during each afternoon--1400 to 2000--but levels are relatively constant, day and night, upslope and downslope.

During the three-week intensive period, we did not observe the downslope maximum seen in sulfur in 1985. However, September 1987 (like, in fact, the entire summer) was virtually devoid of the rain that occurred periodically in 1985. Thus the question of transport across the Sierra Nevada from the east on thunderstorms and fronts must await future studies.

Potassium is a tracer of soil, when coarse, and smoke, when fine (Figure 13 and 28). It is somewhat finer than sulfur, but is remarkable for peaking on both downslope night winds--0200 to 0800--and upslope afternoon winds--1400 to 2200. The afternoon mode is finer than the nighttime mode. There is also a very small coarse soil mode evident in the 2.1 to 4.2 μm regime. Our working hypothesis is that two smoke sources are operational: agricultural burning in the San Joaquin Valley in the afternoon and local campfires at night.

Diurnal particulate cycles: Emerald Lake

The diurnal patterns of the two largest fine-particle components at Emerald Lake appear in Figure 29. From an earlier diagram, Figure 24, it is clear that the synoptic variability at Ash Mountain and Giant Forest is weakened at Emerald Lake. The detailed record confirms this; although a sulfur peak is seen on July 23, it lasts only for 8 hours at Emerald Lake (0000 to 0800 hours), whereas it lingers longer at Giant Forest. A very regular diurnal pattern replaces it, with peak sulfur values in nighttime hours, as at Giant Forest. A high correlation exists between S and K. (K is generally a smoke tracer, but also occurs in soils.)

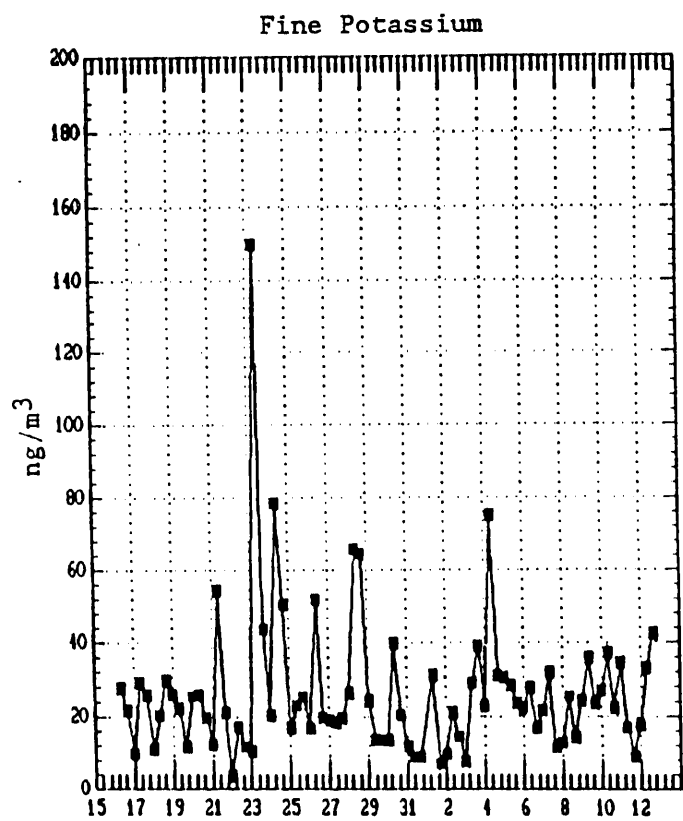
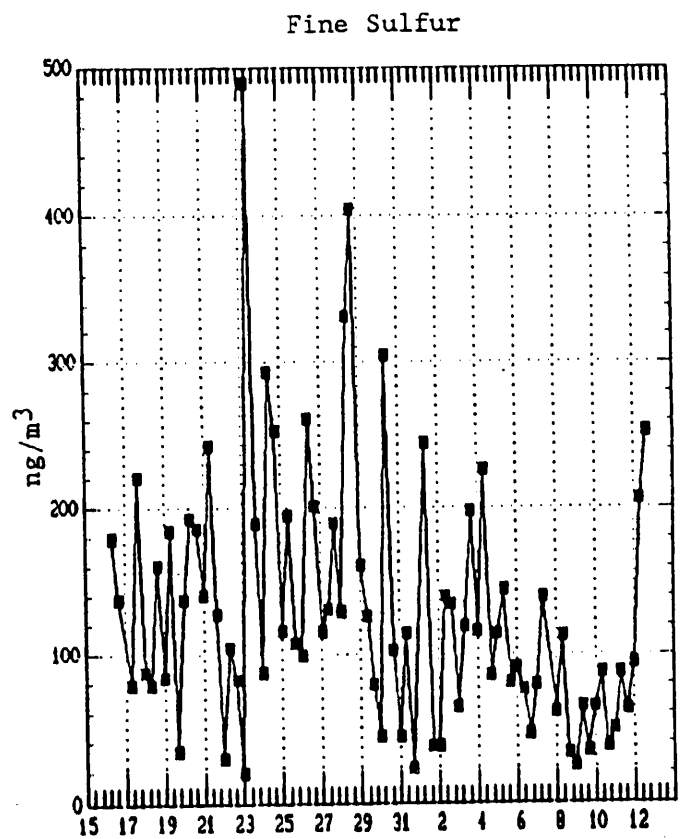


Figure 29: Fine sulfur and fine potassium (SPASI) at Emerald Lake, July and August, 1985

PARTICLE DEPOSITION

Dry deposition removal of particulate matter from the atmosphere is often characterized mathematically as the product of the deposition velocity and the ambient concentration. Measurements of the ambient concentrations can be obtained by any of a number of well-documented procedures. The deposition velocity, however, is much more difficult to determine.

Other, more expensive means of measuring deposition include mass-balance measurement of the ambient particulate concentration gradient and micrometeorological measurement of eddy flux. These procedures require more sophisticated measurement techniques than those employed in this study.

Most commonly resistance summations are used today to predict deposition velocities. Calculation of gravity-settling velocity, Brownian diffusion, and turbulent transport mechanisms of overcoming these resistances can also be used in prediction, deposition velocities. In all cases dry deposition velocity is equal to or greater than the gravity-settling velocity (Schmell 1980). For particles greater than 10 μm , gravity-settling velocity is dominant. For particles less than 0.1 μm , diffusion becomes the dominant means of deposition. In addition, but seldom accounted for, a number of other factors influence the rate of deposition. These factors include electrophoretic and thermophoretic forces, humidity gradients, the hydrophilicity of the particle, and the nature and roughness of the deposition surface and other boundary layer properties (Schmell 1980).

Deposition velocities (V_d) are frequently determined from field data as the deposition flux to a surface (F) divided by the ambient concentration (C), usually at a reference height of 1-1.5m.

$$\dot{V}_d = \frac{F}{C} \quad (1)$$

Since the deposition velocity is a function of particle size, equation 1 is more proper for monodisperse aerosols. For polydisperse aerosols found in ambient conditions, equation 2 is useful:

$$V_d = \frac{\sum V_{di} * C_i}{\sum C_i} \quad (2)$$

where V_{di} and C_i are the deposition velocities and concentrations of the i^{th} size particles (Sehmel 1980). Figure 30 and Table 8 list the deposition velocities associated with the DRUM samples.

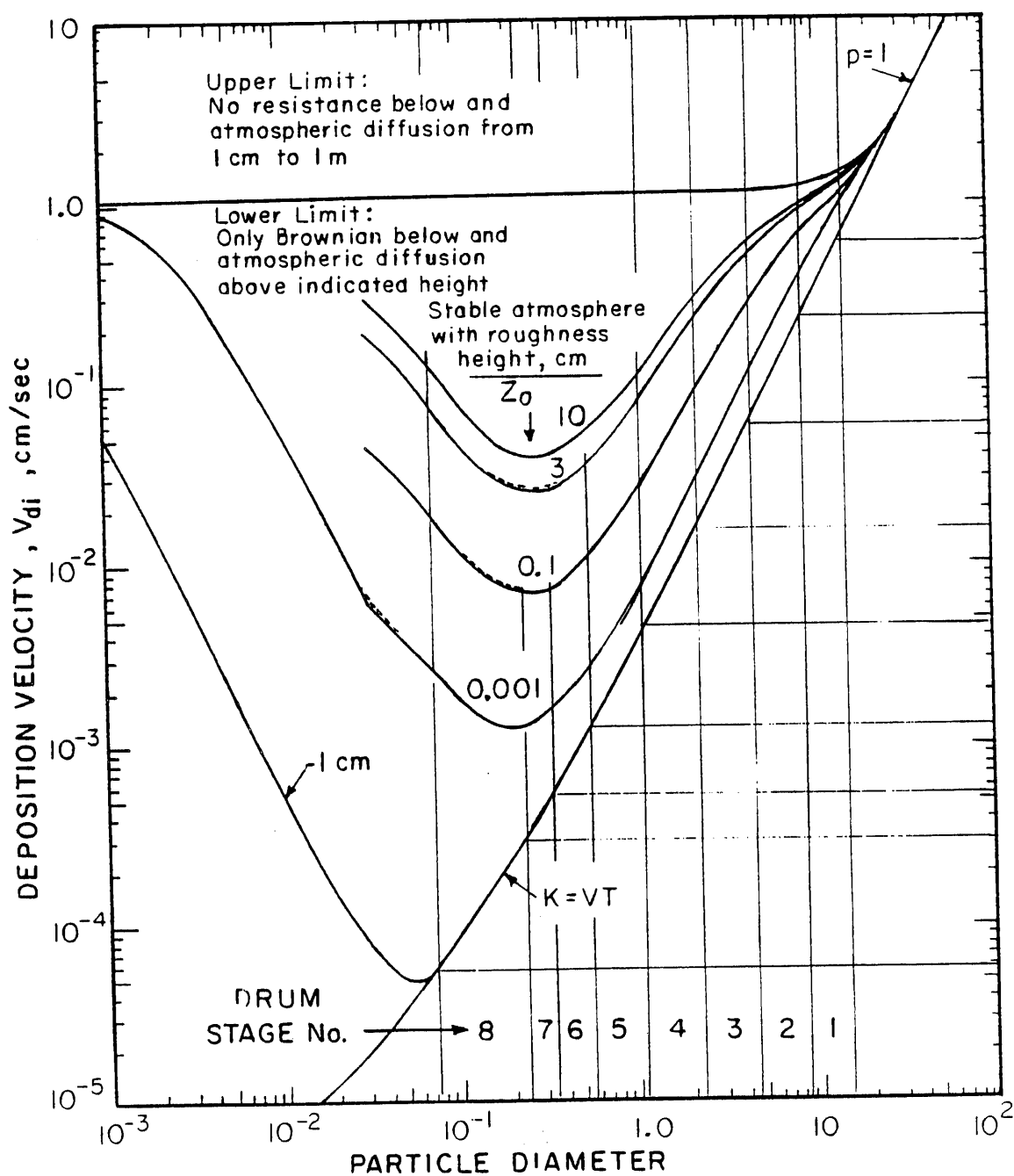


Figure 30: DRUM sampler stages vs deposition velocity (patterned after Schmell 1980)

Table 8: DRUM sampler particle size, deposition velocity (from Figure 30, $Z_o = 10$), and gravity-settling (V_{TS}), and diffusional velocity (D)

STAGE	PARTICLE SIZE RANGE(μm)	$V_d(\text{cm/s})$	AVE: $V_{TS}(\text{cm/s})$	AVE:D(cm/s)
1	13.00-8.50	1.265	3.64×10^{-1}	2.34×10^{-8}
2	8.50-4.30	0.724	1.38×10^{-1}	4.28×10^{-8}
3	4.30-2.10	0.424	3.56×10^{-2}	8.96×10^{-8}
4	2.10-1.15	0.199	9.30×10^{-3}	1.78×10^{-7}
5	1.15-0.56	0.084	2.86×10^{-3}	4.33×10^{-7}
6	0.56-0.34	0.046	8.62×10^{-4}	8.36×10^{-7}
7	0.34-0.24	0.040	4.04×10^{-4}	1.36×10^{-6}
8	0.24-0.07	0.078	1.74×10^{-4}	7.20×10^{-6}

Deposition velocities for several elements were calculated by equations using DRUM sample elemental data and theoretical stage deposition velocity (Table 8). These are listed in Table 9 and compares to the deposition velocity from surrogate surfaces.

Table 9: Deposition velocities calculated from DRUM sampler elemental and theoretical deposition velocity data (Table 8); and deposition velocities calculated from flux to a teflon surface and measured ambient particulate elemental data (by SFU sampler)

ELEMENT	$V_d(\text{DRUM})(\text{cm/s})$	$V_d(\text{Surface/SFU})(\text{cm/s})$
S	0.196	0.091
K	0.171	0.741
Si	2.415	0.305
Fe	1.401	0.271
Ca	2.410	0.374

Except for potassium there is good agreement between the deposition velocities calculated from DRUM data or from SFU and deposition surface data. Since the potassium is likely to come from local campfires, ongoing forest fires and other smoke sources, the deposition surfaces received potassium associated with very large organic rich, smoke particles which were excluded by the inlet of the DRUM or SFU sampler. This would cause the higher deposition velocity in the deposition surface calculations. For the DRUM sampler, sulfur and potassium are both on small particles with peak concentrations in Stage 6, which the soil elements (Si, Fe, Ca) are on larger particles with peak concentrations in Stage 3. The soil elements have similar deposition velocities both within each calculation method and between the calculation methods. That the V_d is lower on the surrogate surfaces could be due to incomplete retention on the surface.

DRY DEPOSITION

Because of the scarcity of summer rainfall in California, dry deposition constitutes the major route of exposure to air pollutants for plants during the growing season. We have observed that needles of Jeffrey pine trees at Giant Forest show considerable damage to their upper surfaces. Such damage is consistent with dry deposition of acidic pollutants (winter ice damage to the needles also mostly affects the upper surfaces). Since a large portion of the Jeffrey pines at this elevation show heavy damage (needle loss, tip bunching, etc.), the mechanisms of dry deposition and its impact on the vegetation should be studied. Therefore, although it was not included in the original research plan, we undertook to devise a means of measuring the dry deposition.

Method of collection

On August 14, 1987, several dry deposition surrogate surfaces were placed at the Giant Forest sampling site and exposed for four days, during which time no rainfall occurred. The surrogate surfaces exposed were wax-coated, K_2CO_3 coated (for SO_2 collection), and uncoated stretched teflon filters (Gelman Sciences, 37 mm Teflon PTFE Membrane, 2 μ m pore size). Because of uncertainties in measuring the amount of coating material and difficulties in obtaining a uniform coating, these coated filters proved unsatisfactory. Also, the wax coating tended to evaporate during exposure, thereby confounding mass and elemental analysis. Therefore only data from the uncoated filters are presented here.

Stretched teflon filters were preweighed and mounted in plastic 35-mm slide frames. The slides were then attached approximately 13.5 cm from a wooden axis by short wooden slats glued to the axis and the slide frame and placed approximately 13.5 cm apart. This array was then mounted on wooden legs approximately 75 cm above bare rock ground. The deposition surface array was placed so that it was neither influenced by other instruments at the site, nor influenced them.

On August 18, 1987, after 98 hours of exposure, the surfaces were recovered and placed in individual containers for transport to Davis for analysis. At the laboratory the filters were removed from the slide frames and post-weighed. Next they were remounted in their slide frames for PIXE analysis of elemental content. The results of PIXE analysis of the deposition slides and of the ambient aerosol, as measured by SFU samplers, were used to calculate the deposition velocity by the flux-concentration method, using the following equation

$$V_d = F/C.$$

Results of dry deposition tests

Figure 31 illustrates the average ambient aerosol elemental composition, as measured by SFU sampling, during the exposure period of the dry deposition slides.

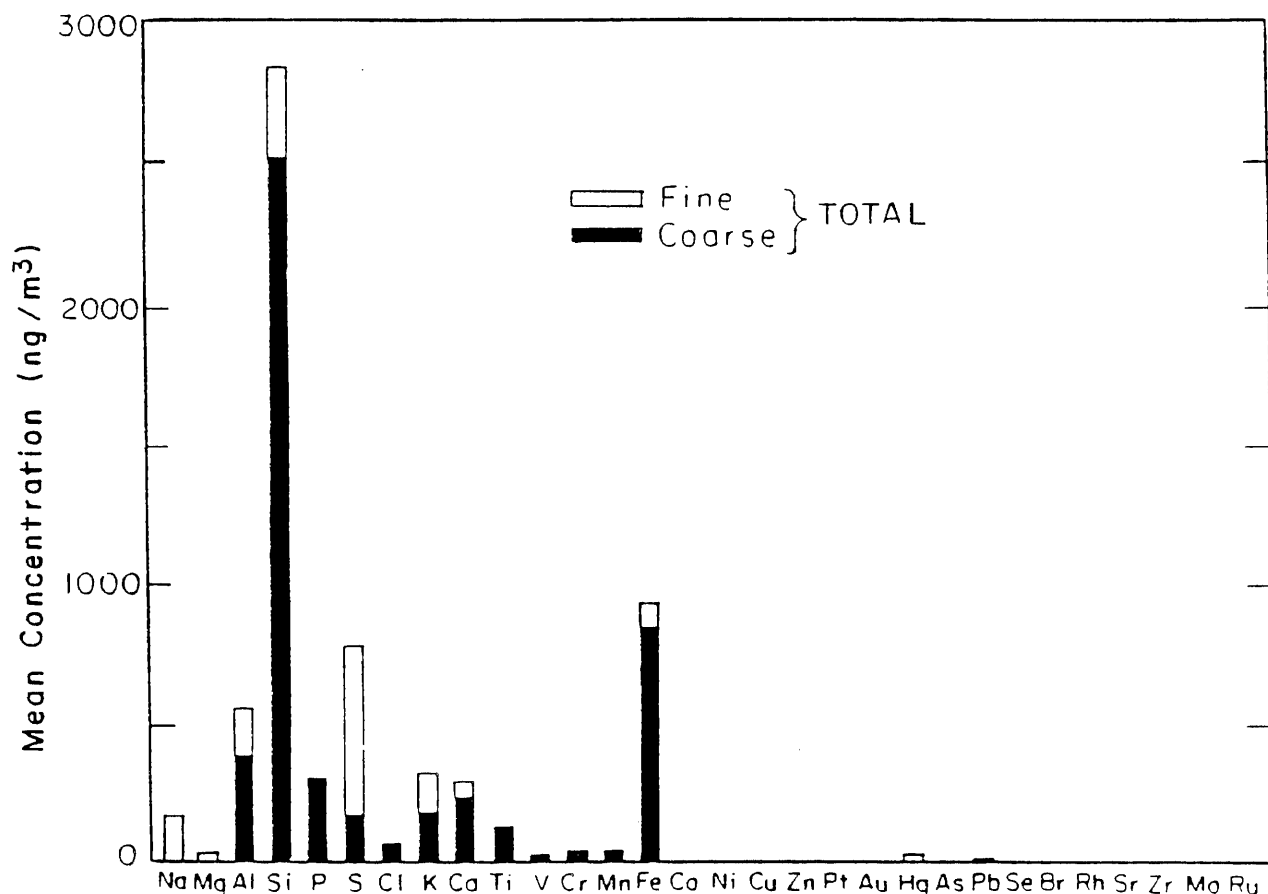


Figure 31: Ambient particulate concentration at Giant Forest, August 14-18, 1987 (ng/m³). Fine fraction <2.5 μ m, coarse fraction 10-2.5 μ m

The data are divided into coarse (10-2.5 μ m) and fine (<2.5 μ m) particle-size fractions. Silicon and iron are the dominant elements in the coarse stage, while sulfur is the largest contributor to the fine stage. A potassium-to-calcium ratio of 2.51 in the fine stage (0.77 in the coarse stage) indicates an important influence of smoke on the air quality at the site. The Giant Forest site is not far from the park lodge and an area of camping cabins where wood burns for heating and cooking, generating significant amounts of wood smoke.

As observed in the DRUM sampler data discussed previously, the soil particles are predominantly in Stage 3 (2-4 μ m), rather than the usual Stage 1 (8-10 μ m). The smaller size of the particles reduces the flux to surfaces (and hence reduces the deposition velocity) of the generally buffering soil particles, resulting in a possible enhancement of the effects of the more acidic anthropogenic fine aerosols. It appears that the soil particles seen in Sequoia National Park are predominantly aged particles derived from the Central Valley, the large size fractions of which have settled out during transport to the park.

Figure 32 illustrates the elemental deposition to the surfaces after 98 hours of exposure.

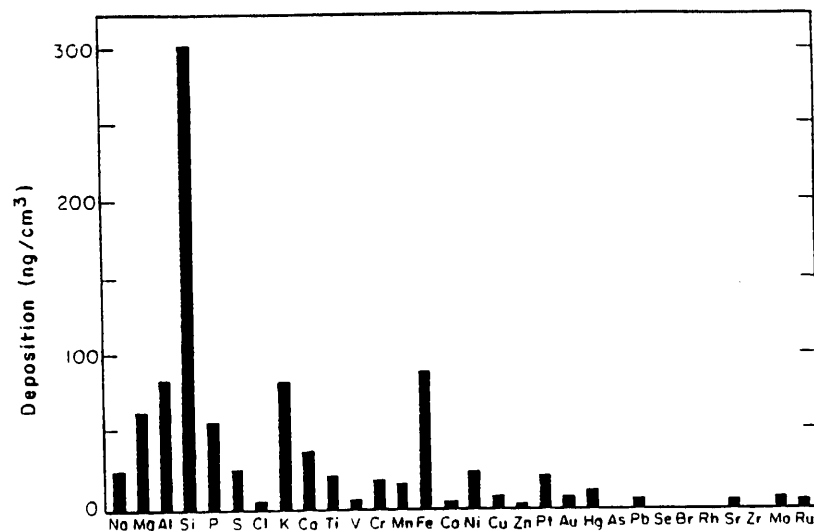


Figure 32: Elemental deposition to stretched teflon filter surrogate surface August 14-18, 1987 (ng/cm²)

On the deposition surfaces, silicon again dominates followed by iron, aluminium, and potassium. The influence of smoke on the deposition surfaces is again evidenced by the high potassium level and a K:Ca ratio of 2.23.

The deposition velocities for the various elements were calculated using the deposition flux and the total less-than-10- μ m ambient concentration data (Table 10). The resulting values substantially agree with the values obtained by various other studies, as reviewed by Sehmel (1980).

A Euclidean distance index of similarity of the deposition velocities was calculated. This similarity index is an algebraic construct which relates the deposition velocity of the element in question and the deposition velocities of the other elements. The similarities are then displayed in a hierarchical manner in a single-link clustered dendrogram (Figure 33). The similarity calculated as one minus the dissimilarity usually presented, is presented for semantic clarity. Similarity ranges from one for elements with identical deposition velocities to 0 if the elements are totally unrelated.

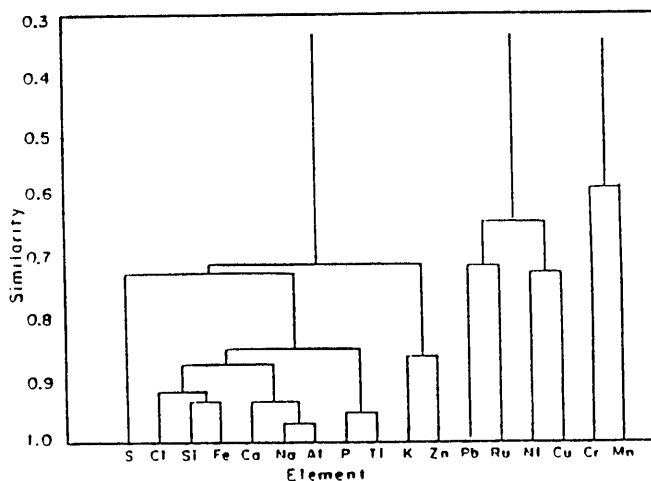


Figure 33: Dendrogram of deposition velocity Euclidean distance measure of similarity

At a similarity of better than 0.89, Cl, Si, Fe, Ca, Na, Al, and Ti form a grouping of largely naturally occurring species. The more anthropogenic elements (sulfur, potassium, and zinc) join this group in a range between approximately 0.73 to 0.79.

Recalculating the elemental values from the PIXE analysis in terms of ionic micro-equivalent fluxes, e.g. sulfur in terms of sulfate ions (tables 11 and 12), reveals general agreement with other deposition studies made at Emerald Lake in Sequoia and elsewhere in southern California (Bytnerowicz and Olszyk 1988).

Table 10: Deposition velocity (cm/s)

ELEMENT	DEPOSITION VELOCITY	ELEMENT	DEPOSITION VELOCITY
Na	.408	Ni	3.289
Mg	5.440	Cu	3.149
Al	.425	Zn	.671
Si	.305	Pl	2.684
P	.526	Au	4.156
S	.091	Hg	1.951
Cl	.230	As	0
K	.741	Pb	2.822
Ca	.374	Se	0
Ti	.502	Br	0
U	1.108	Rb	0
Cr	1.432	Sr	28.345
Mn	1.642	Zr	0
Fe	.271	Mo	0
Co	0	Ru	2.967

Table 11: Ionic deposition flux ($\mu\text{Eq m}^{-2}\text{h}^{-1}$). Giant Forest values calculated from elemental data; Emerald Lake from Bytnerowicz and Olszyk, 1988

ION	EMERALD LAKE (NYLON)	EMERALD LAKE (PAPER)	EMERALD LAKE (AVERAGE)	GIANT FOREST (TEFLON)
SO ₄ (2-)	.069	.157	.133	.159
PO ₄ (3-)	0	0	0	.562
Cl (1-)	1.863	.345	1.104	.014
Ca (2+)	.781	.504	.642	.190
Mg (2+)	.053	.021	.037	.526
Na (1+)	1.179	1.554	1.366	.104
Zn (2+)	.031	.021	.026	.009
Fe (3+)	.080	.050	.065	.491
Mn (2+)	.007	.005	.006	.059
Pb (2+)	.055	.055	.055	.007

<u>LOCATION</u>	<u>NYLON</u>	<u>PAPER</u>	<u>TEFLON</u>
EASTERN BROOK LAKE	0.012	0.126	ns
EMERALD LAKE	0.069	0.157	ns
TANBARK FLATS	1.703	0.137	ns
GIANT FOREST	ns	ns	0.159

ns = no sample

Table 12: Sulfate deposition flux ($\mu\text{Eq m}^{-2}\text{h}^{-1}$). Giant Forest values calculated from elemental data; other sites from Bytnerowicz and Olszyk, 1988.

The Giant Forest site, being in the midst of the park's tourist attractions, is heavily influenced by local sources. Emerald Lake, conversely, is a high altitude site generally above the mixing level (Giant Forest usually is at or below the summer mixing level) and less subject to local sources, so that only general comparisons between Giant Forest and Emerald Lake depositions are possible.

Conclusions of dry deposition tests

Study results demonstrate the merits of PIXE analysis of dry deposition for viewing a wide spectrum of elemental deposition. We feel that further deployment of teflon filter surrogate surfaces as monitoring tools would prove useful. Additionally, we recommend undertaking studies to determine the fate of dry deposition elements in the plant systems (uptake, status, and cycling of nutrients in the forest).

The extremely simple procedures used to measure dry deposition gave good results, as indicated by the agreement between the ionic fluxes calculated and those seen by Bytnerowicz and Olszyk (1988) in other areas of the park and southern California. The agreement of the deposition velocities in this study with those reported by Sehmel (1980) in his review also supports our results. Moreover, that we report deposition fluxes and deposition velocities for a wide spectrum of elements increases the value of the method we used.

WET DEPOSITION

During the 1987 study, no significant rainfall occurred; therefore, wet deposition was not an important factor. A brief discussion of 1985 rainfall in Sequoia is included here as an example of possible wet deposition impact. The 1985 storms showed 3 general patterns of storm type and direction of approach: frontal synoptic storms from the west; southerly storms, often thunderstorms; and northerly frontal storms. These weather system storms are separate from the local geographic and diurnal heat-induced thunderstorms.

Four major rain periods occurred during summer 1985: July 25 and 26, September 4 and 5, September 10 and 11, and October 8 and 9. During these periods, the pH values ranged from 4.27 to 5.44. The behavior of fine particles was highly variable, but three different patterns emerged, corresponding to the three storm patterns (Table 13).

Frontal synoptic storms

Generally, frontal synoptic storms from the west (July 25-26, 1985) have low fluxes of SO_4 , NO_3 , and hydrogen ion. Sulfur particulate values decreased, and dissolved nitrate values were highest relative to SO_4 in this type of storm. The source appears to be the central San Joaquin Valley.

Southerly storms

Southerly storms, often thunderstorms, are associated with low pressure in Nevada (September 4-5 and September 10-11, 1985). These storms have high fluxes of SO_4 , NO_3 , and H ion. Sulfur particulates increased as the storm arrived (along with Ni). Clearly, the storm was carrying a considerable burden of pollutants, some as aerosol and some incorporated into rainfall. Arsenic, a virtually unique tracer of copper smelters, was seen in particles during one storm. A sub-tropical air mass moved northward through the area, transporting pollutants from Arizona, the Colorado River Basin, and perhaps the southern San Joaquin Valley, as shown in the Ni tracer.

Northerly frontal storms

The northerly frontal storm of October 8-9, 1985, was a north Pacific storm bearing mostly clean air (and a little salt). It had an intermediate level of SO_4 and NO_3 , possibly picked up across the San Francisco Bay area and northern California. The pH was the highest of all storms, 5.44 (essentially the CO_2 buffered value, thus clean). Very high hydrogen:sulfur ratios occurred in the rainfall, and this storm had a low NO_3 level relative to SO_4 in the rain.

The dominant SO_4^{2-} , NO_3^- , and H fluxes in wet deposition come from sources south and east of Sequoia. Although the storm cells move in from the south and east, they can also entrain air from the west that has been transported at low elevation. This may mix sources in a single storm.

Table 13: Giant Forest rain events, 1985

	July 25/26	Sept 4/5	Sept 11	Oct 8/9
Rain (cm)	0.20(0.11)	1.29(0.09)	3.94	0.93(1.16)
pH	4.85(4.27)	4.65(4.45)	4.85	4.81(5.44)
Fluxes* H	28(59)	288(18)	556	144(42)
SO ₄ /NO ₃	6.8/5.0	36.1/19.9	96.1/55.2	38.7/18.3
S particulates†	decreased 800/486/712	increased 288/358/530	increased 425/623/420	decreased 566/308/290
Ratio H/S particulates†	1.1/.9/1.1	.9/.7/.8	.6/1.2/.8	1.5/1.8/2.0

RAIN (ratio to SO₄)

H	0.4%	0.8%	0.6%	3.7%
NO ₃	74%	55%	57%	47%
NH ₄	28%	20%	22%	16%
Cl	10%	4%	9%	7%
Na	10%	4%	9%	7%
K	20%	3%	1%	5%
Ca	1%	4%	26%	6%
Mg	1%	4%	26%	6%

PARTICLES

Increased	Br, Cu	S, Ni	S, Ni, Zn, Br, Pb, Na Soil, (H)	Cl, (H)
Decreased	S, K, Pb	Na, soil Zn, K, (H)	none	Na, K, soil

METEOROLOGY

Frontal, from west	Nevada Low pressure	Nevada Low pressure	Frontal, from north
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() Figures in parenthesis refer to the second day of rainfall

* Fluxes, μ equiv./m² per event

** ng/m³ aerosol

† 3 measurements per rain event

Meteorology of a rainy period

The particulate and wet deposition sulfur species during the rain which began September 10, 1985 were associated, as evidenced by a sharp increase in particulate sulfur at precisely the beginning of rainfall at the Giant Forest site (Figure 34). This type of rain event, unlike the frontal systems, brings high particulate sulfur concentrations to Giant Forest. We should also note that thunderstorm rain events are much more common east of Giant Forest, even at Emerald Lake, since the Giant Forest site lies west of the "Great Western Divide" and is separated by the upper Kern River Valley from the main ridge of the Sierra Nevada.

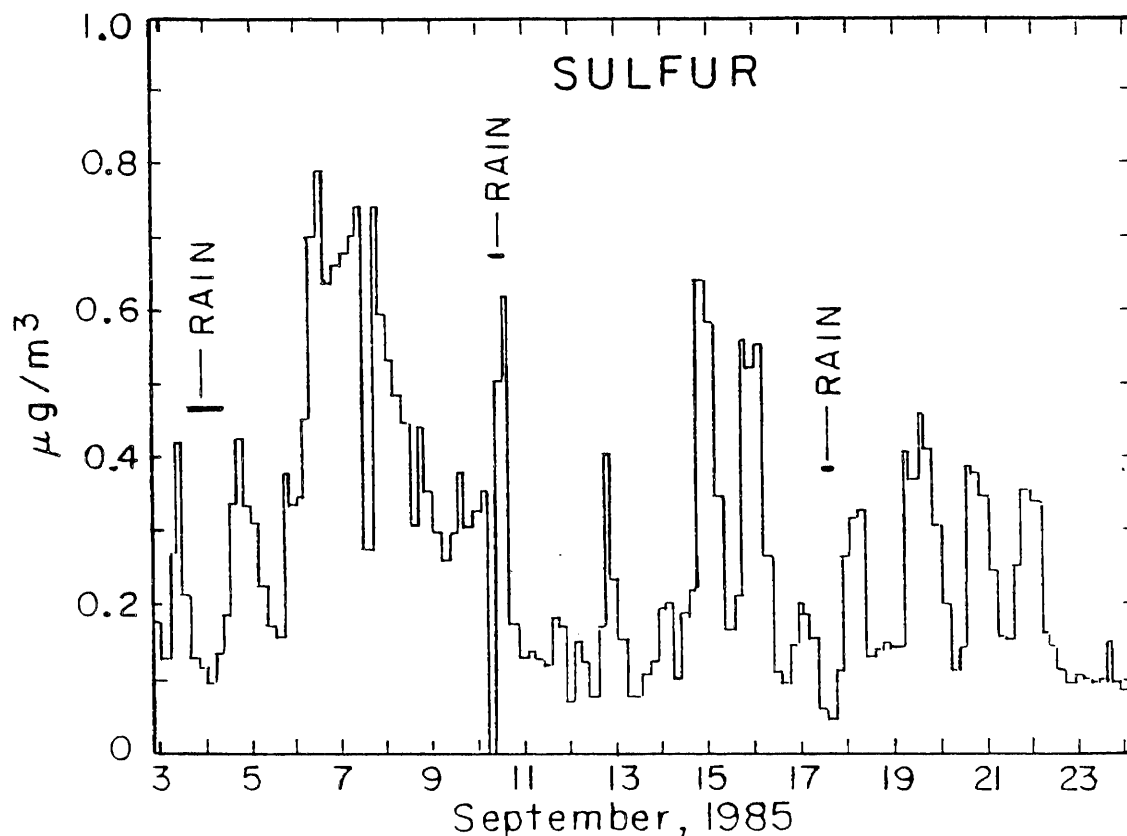


Figure 34 Sulfur concentrations, DRUM stage 6, at Giant Forest, 10-24 September 1985

OZONE MONITORING

We are not aware of any previous efforts to measure ozone on a continuous basis in an area as remote as Emerald Lake. Solar-powered ozone monitors have been operated before (and are currently in operation), but only at sites which are accessible by road. Access to the Emerald Lake area was very restricted. The lake can be reached on foot or by helicopter, although helicopter access is limited to the beginning and end of the summer visitor season. Further, the ozone monitor, solar panel array, and associated equipment had to have only a minimal visual impact on the landscape.

We chose to use an ozone monitor which was designed for industrial hygiene applications. This unit (CSI, model 2000) is portable (22 lbs), uses 12 VDC electricity, and has been designated by the U.S. Environmental Protection Agency as an ozone reference method (CSI 1978). It is a chemiluminescent-type monitor which measures ozone concentration by reacting ethylene gas with ozone in a reaction chamber. The light produced by the ethylene/ozone reaction is detected by a photomultiplier tube and is proportional to ozone concentration. Because it was necessary to transport the equipment by helicopter, we ordered an ozone monitor modified to use Ethychem, a non-flammable, proprietary mixture of ethylene and carbon dioxide.

Table 1 shows the ozone monitor operating periods. The monitor was first operated at the Emerald ridge site for 18 days in September 1986. The solar power system used with the monitor during this period had been designed on the basis of the manufacturer's power requirement specifications. These specifications were optimistic, however, and did not account for the increased power consumption needed to control instrument temperature at ambient temperatures above or below 25 C (77 F). Because this time period was cold and frequently cloudy, the monitor operated only intermittently. We will not present or discuss the limited data obtained; the discussion below refers only to monitor operation during 1987.

Below we discuss (1) the solar-powered ozone monitoring station, (2) the ozone monitor calibration and associated problems, (3) the Emerald Lake ozone data in comparison to ozone data from the two other monitors in Sequoia at Ash Mountain and Giant Forest, as well as from the CARB's ozone monitor in Visalia, (4) our interpretation of the ozone results, and (5) our recommendations regarding ozone monitoring at remote sites.

Solar-powered ozone monitoring station

This section describes the station as it operated during summer 1987. Power was provided by four solar panels (ARCO, model M75) which had a total area of 1.6 square meters and a combined peak output of 188 watts. A regulator (Sunselector Junior, Bobier Electronics) controlled the charging of four 12-volt deep-discharge-type storage batteries rated at 105 amp-hours each (GNB, model ST154). This solar-powered system provided power for the ozone monitor and data logger, as well as the solar-powered SFU sampler, meteorological instruments, and auxiliary equipment.

The data logger (Omnidata International, Easylogger model) recorded the ozone concentration and the ozone monitor's sample air flow rate, internal fault indicator, and cabinet temperature, and the supply voltage from the

solar-power system. (This same data logger also supported the meteorological instruments and solar SFU sampler.) Data were stored on EPROM (erasable programmable memory) packs which held one week of data. The packs were replaced weekly by a field technician and mailed back to U.C. Davis, where they were downloaded to a microcomputer and stored on disks. The operation of the ozone monitor, data logger, and other equipment was checked thoroughly by the technician at least once per week.

Calibration

The operation of a solar-powered ozone monitoring system at high elevation at Emerald Lake involved the application of new and innovative techniques. However, the operation was not without problems. Problems of span change during the monitoring period, problems with making the necessary altitude corrections, and the effects of large temperature changes in the instrument shelter all suggest that an uncertainty should be applied to the ozone concentrations at Emerald Lake. This uncertainty is shown in the mean ozone values in Table 13 of 0.017-0.033 ppmv. This uncertainty is substantial on a percentage basis but relatively small on an absolute basis (0.016 ppmv).

Table 14: Ozone statistics summary for 4 sites.

<u>Site</u>	<u>Mean Concentration (ppmv)</u>	<u>California Standard Exceedance Hours</u>	<u>Data Hours</u>
Emerald Lake	0.017-0.033	0	1156
Giant Forest	0.068	123	1405
Ash Mountain	0.080	320	1364
Visalia	0.050	118	1295

Note: Data are for July 27 - September 24, 1987;
Total possible data hours = 1440

Results

Figure 35a shows the ozone concentration at Emerald Lake during the entire operating period: July 27-September 24, 1987 (days 207-266). The curve is based on mean hourly concentrations; the gaps are due to missing data. The peak concentration observed, given the range of span values stated above, was 0.03-0.06 ppmv. The lowest concentration observed was 0.005-0.01 ppmv. The mean concentration was 0.017-0.033 ppmv; however, this is biased low because most missing data occurred during afternoons when concentrations were likely to be highest.

Figures 35b, c, and d show summer 1987 ozone data for Giant Forest, Ash Mountain, and Visalia, respectively. A summary of ozone statistics for the four sites appears in Table 15. Note that figures 35b-d show data for July 20-September 27 (days 200-269), but the statistics are based only on July 27-September 24 (days 207-266), the 60-day period when the Emerald Lake ozone monitor was operating. Of the four sites, Ash Mountain had the highest mean ozone concentration and highest number of hours exceeding California's current ozone standard. Giant Forest was second in both mean concentration and exceedance hours, Visalia was third, and Emerald Lake was fourth. The amplitude of the diurnal concentration cycle was greatest at Visalia and least at Emerald Lake. As expected, Visalia experienced both the highest and lowest ozone concentrations of the four sites: hourly mean levels reached 0.15 ppmv twice and were 0 ppmv for several hours.

Table 15: Time of maximum and minimum ozone concentrations at 4 sites

<u>Site</u>	<u>Mean Hours of Maximum Ozone Concentration</u>	<u>Mean Hour of Minimum Ozone Concentration</u>
Visalia	1500	0500
Ash Mountain	1800	0600-0700
Giant Forest	1700	0800
Emerald Lake	1900	1000

Note: Based on ozone data for (July 27 - September 24, 1987); All times PST

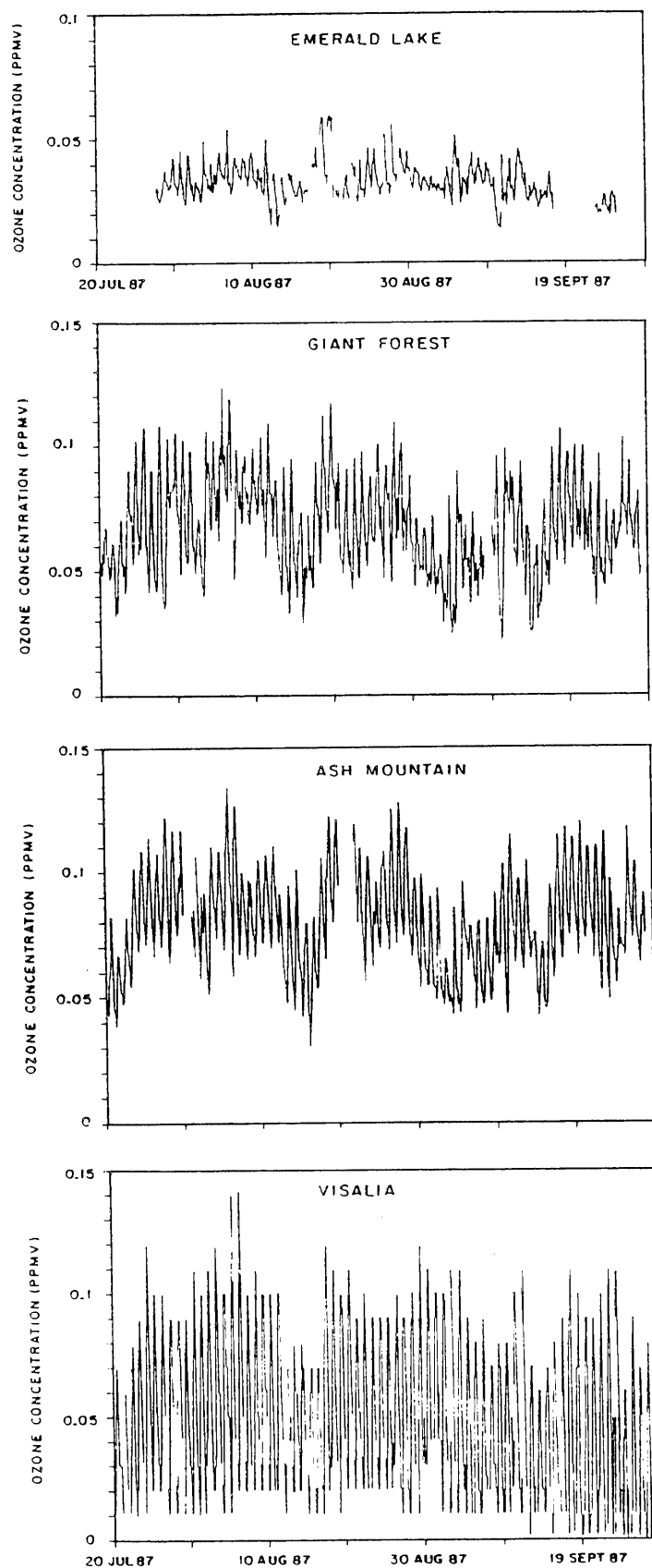


Figure 35 a,b,c,d: Diurnal variations, ozone vs elevation, summer, 1987
(July 20-September 26)

Figures 36-38 depict the ozone data at Emerald Lake, Ash Mountain, and Visalia in relation to Giant Forest. Figure 36 shows that while some correlation exists between the Emerald Lake and Giant Forest ozone data, the levels at Emerald lake are greatly diminished. The ozone levels at Ash Mountain and Giant Forest, as seen in figure 37, are both correlated and of approximately the same value. Figure 38 reflects the approximately 1 to 1 correspondence of ozone levels at Visalia and Giant Forest and also the high variability of the Visalia ozone concentrations.

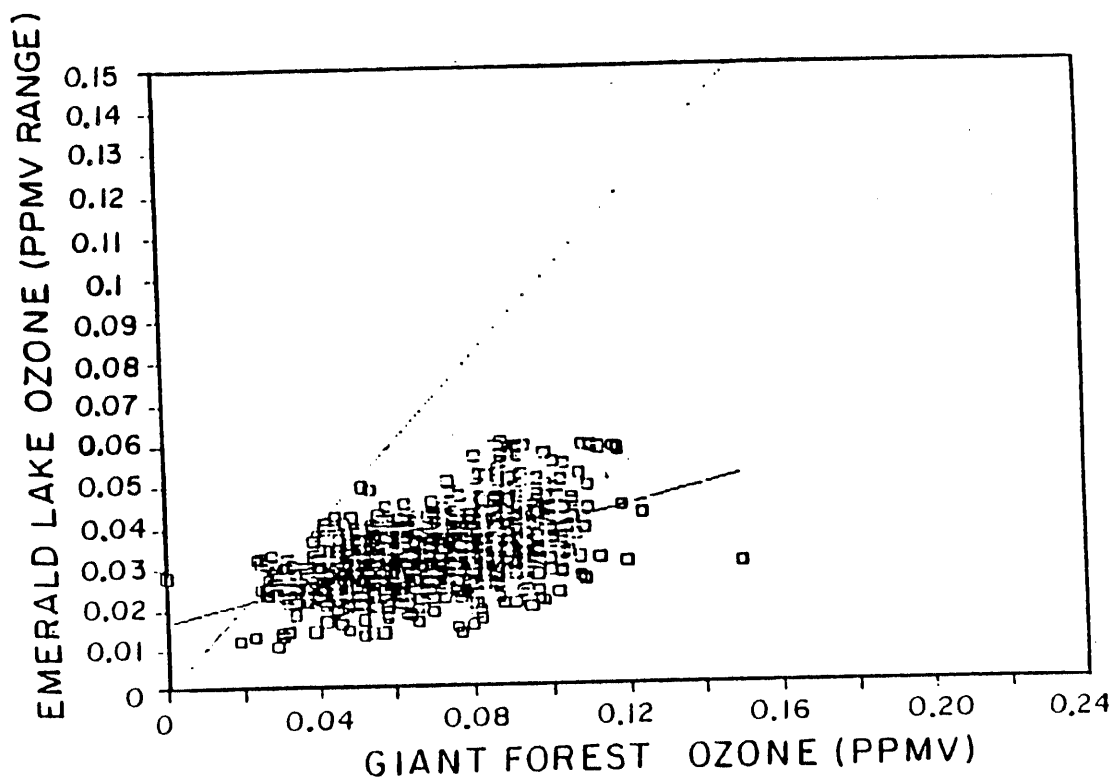


Figure 36: Scatter plot, ozone, Emerald Lake vs Giant Forest

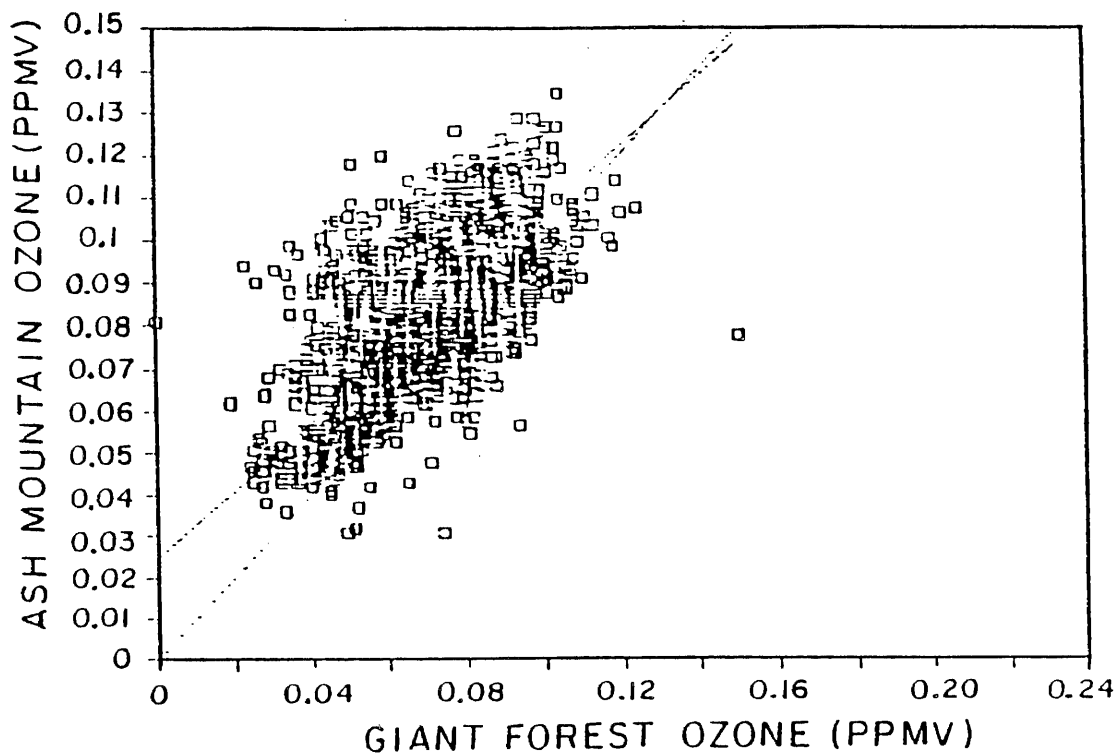


Figure 37: Scatter plot, ozone, Ash Mountain vs Giant Forest

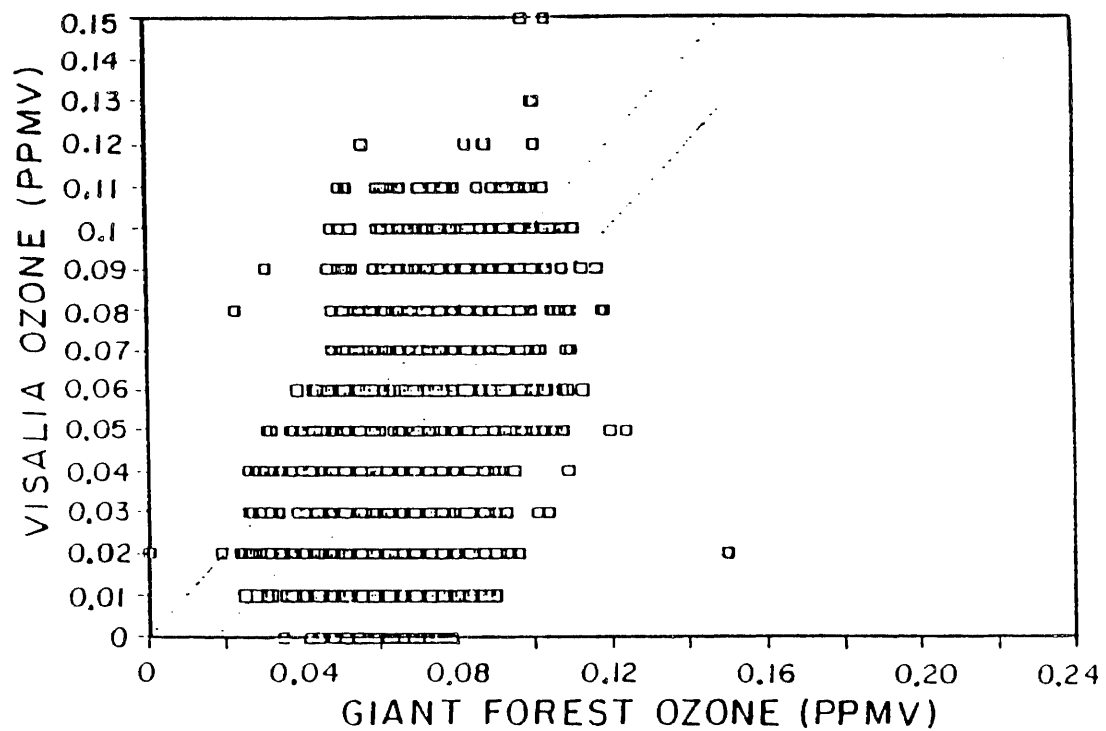


Figure 38: Scatter plot, ozone, Visalia vs Giant Forest

Mean hourly ozone concentrations at the four sites are presented by hour in Figure 39 (all times presented here are Pacific Standard Time). The curves are based on data for the same 60-day period as above [July 27-September 24].

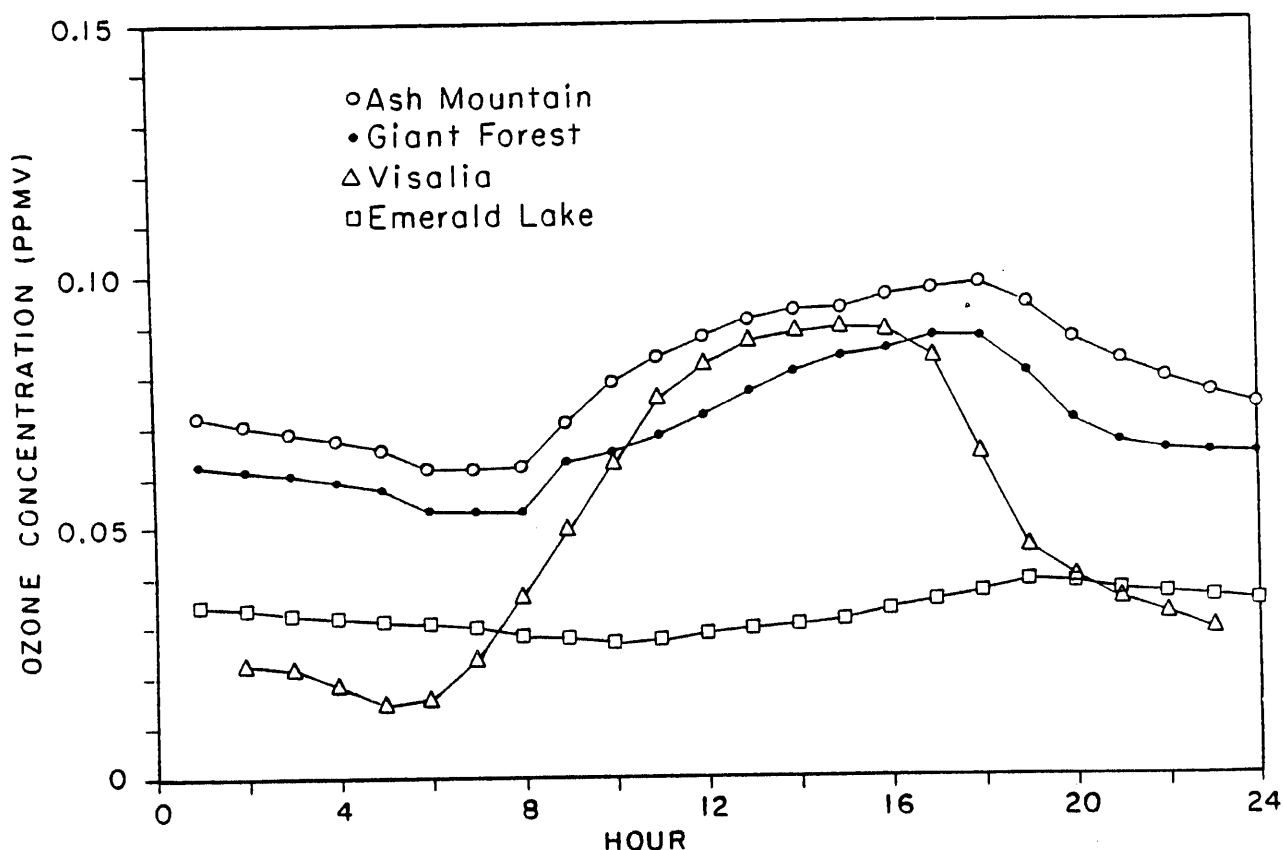


Figure 39: Mean diurnal variations of ozone vs elevation

There were two significantly different (30%) ozone calibration values for the instrument during the study. Note that the higher of the two calibration values has been used for the Emerald Lake data, so the actual data could be somewhat lower.

The diurnal ozone concentration cycle is apparent for all four sites even though the curves represent 60-day means. This figure clearly shows the phase-differences in the diurnal cycles of the four sites. The mean times of maximum and minimum ozone concentration are listed in Table 15. Maximum and minimum ozone levels were reached progressively later each day as site elevation increased. The only exception to this trend was the time of maximum concentration at Ash Mountain and Giant Forest. There was 4 hours' difference between the times of maximum concentration at Visalia and at Emerald Lake, and 5 hours' difference between the times of minimum concentration at these two sites.

Statistical analyses were applied to the daily maximum-hour ozone values at Visalia, Ash Mountain, Giant Forest, Emerald Lake. Highest mean ozone concentrations were at Ash Mountain (0.103 ppmv) while the highest maximum ozone concentration was at Visalia (0.150 ppmv). Mean concentrations at

Emerald Lake were 0.034 ppmv, less than 38% of the values at the other locations.

The correlation matrix shows high correlation between Ash Mountain and Giant Forest ($r=0.88$), lower correlation between Visalia and Ash Mountain/Giant Forest ($r=0.33-0.34$), and low correlations between Emerald Lake and the other three sites ($r=0.02-0.19$).

These data indicate that average daily maximum-hour ozone values are higher at Ash Mountain (0.103 ppmv) on the Sierra slopes than at Visalia (0.095 ppmv) on the valley floor. Furthermore, daily maximum-hour ozone values at Emerald Lake are considerably lower than those measured at lower elevation sites on the Sierra slopes.

Figure 40 relates the valley floor (Visalia) and high mountain (Emerald Lake) extremes of the ozone transect. This figure shows the variability in the levels at the sites and the low correlation.

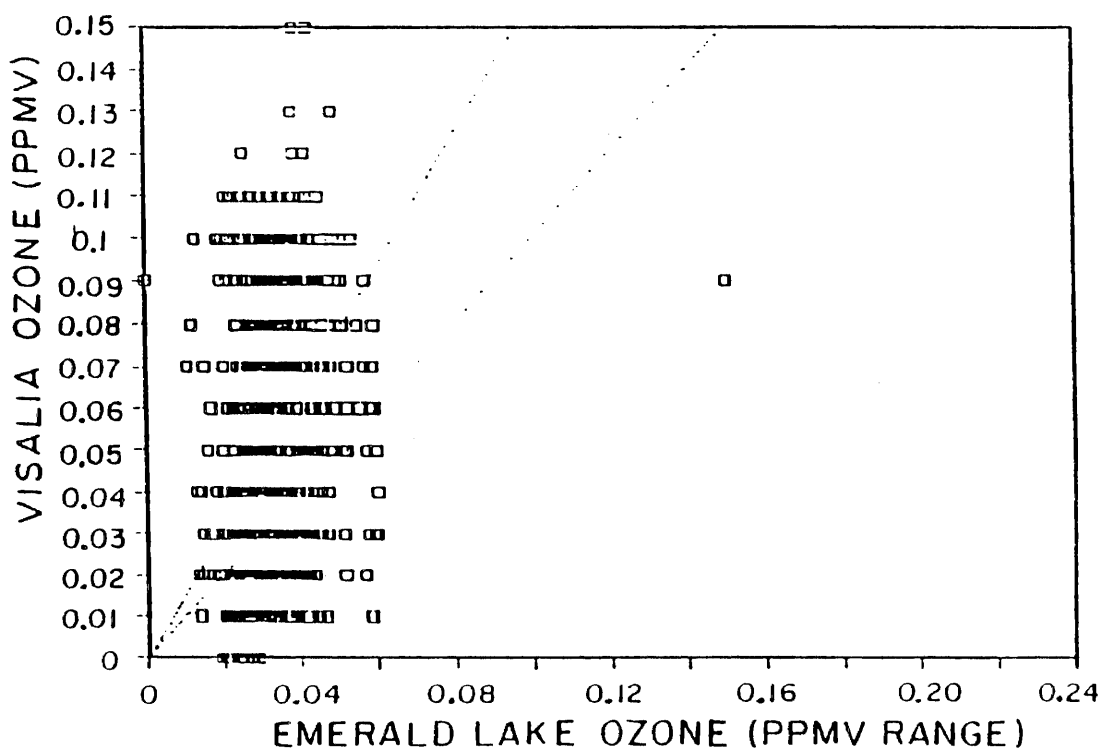


Figure 40: Scatter plot, ozone, Visalia vs Emerald Lake.

Figure 41 shows data for a one-week period at the four sites.

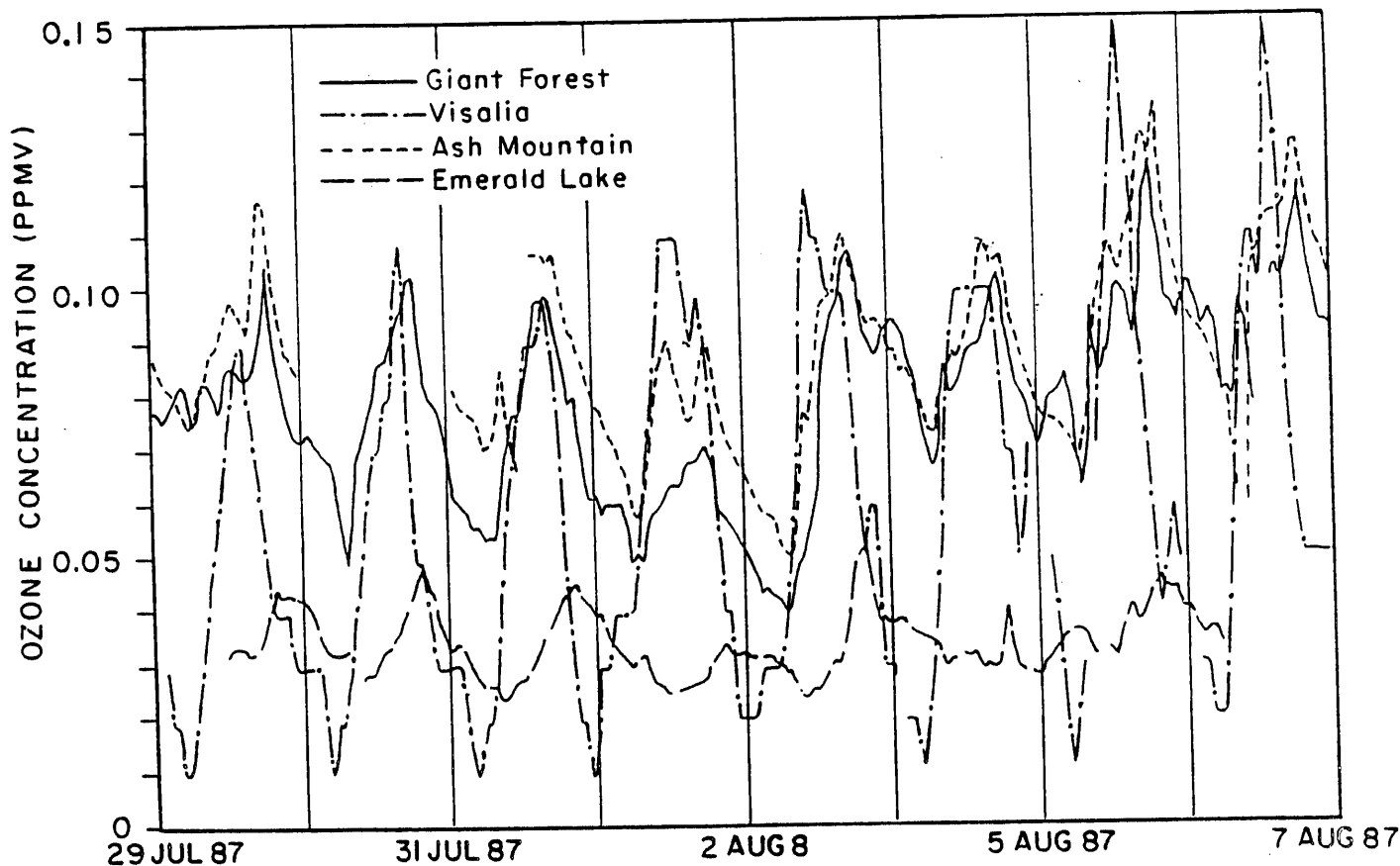


Figure 41: Mean diurnal variations of ozone vs elevation July 29-August 7, 1987

This week was chosen for closer analysis because the data record at all four sites is nearly complete. Other periods are similar. Mean concentrations from noon, July 29 to noon, August 5 were 0.017-0.034, 0.077, 0.087, and 0.060 ppmv for Emerald Lake, Giant Forest, Ash Mountain, and Visalia, respectively. These means are nearly the same as those presented in Table 14 for the entire summer.

The hours of minimum and maximum ozone concentration are shown for 6 diurnal cycles on each of these figures. There is substantial day-to-day variation in the time of minimum and maximum ozone concentrations: as much as 6 hours' difference at Visalia and 3 hours' at Emerald Lake. There is no clear connection in these variations from site to site, however. When a maximum or minimum occurred earlier or later than usual at one site, this deviation was not observed at the other sites.

Wind direction at Emerald Lake typically changed from up-valley to down-valley at 2300-2400 and reversed again at 0700. The wind speeds, typically declined in the afternoon several hours prior to the change in wind direction and did not increase again until after the wind direction changed in the morning. The peak in the diurnal ozone cycle at Emerald Lake appears to have occurred at approximately the same time as the decline in up-valley wind speed. Similarly, the minimum in the diurnal cycle occurred coincident with the return of up-valley winds.

The question of whether ozone concentrations during the summer of 1987 were typical of recent years is addressed by the data in Table 16. These data on California ozone standard exceedance hours at Visalia indicate that ozone levels during summer 1987 were significantly higher than during 1983-85 but less than during 1986 (CARB 1987a).

Table 16: California ozone standard exceedance hours at Visalia: 1983-87

<u>Year</u>	<u>July</u>	<u>August</u>	<u>September</u>	<u>Summer Total</u>
1983	46	20	24	90
1984	46	27	13	86
1985	23	13	10	46
1986	67	151	56	274
1987	31	88	43	162

Discussion

We emphasize that we may draw only cautious conclusions regarding absolute ozone concentrations at Emerald Lake because of the problems with the ozone monitor's calibration described above. However, even our upper estimate of the peak ozone concentration at Emerald Lake during the monitoring period (0.06 ppmv) was significantly less than the California ozone standard (0.09 ppmv). The mean summer ozone concentration measured at Emerald Lake, 0.017-0.033 ppmv, is similar to mean summer concentrations measured at several remote sites in the United States, 0.022-0.040 ppmv (CARB 1987b). These remote sites are thought to be little impacted by anthropogenic ozone. However, none of them is located at an elevation nearly as high as Emerald Lake.

Note that ozone concentrations peaked on average at 1500 PST at Visalia, 1700 PST at Giant Forest, 1800 PST at Ash Mountain, and 1900 PST at Emerald Lake, indicating in general later peaks at higher elevations and suggesting transport of ozone and ozone precursors with the upslope winds.

Table 14, as was evident earlier, shows mean ozone concentrations decreasing (at a minimum) of 0.035 ppmv between Giant Forest and Emerald Lake and 0.012 ppmv between Ash Mountain and Giant Forest. This more rapid decrease in concentrations at the higher elevations has several explanations. First, the semi-permanent temperature inversions which affect much of California during the summer months suppress vertical transport of pollutants through the

inversion. Second, deposition and atmospheric dispersion always reduce pollutant concentrations during transport away from a source, but the most rapid decrease usually occurs near the source. However, dispersion is increased and pollutant concentrations are decreased by convective activity. The granitic surfaces at higher elevations in the Sierra Nevada, generally above the inversion, are heated more rapidly during summer days than the more heavily forested slopes at lower elevations. The formation of cumulus clouds and occasional thunderstorms on the Sierra slopes provides visible evidence of this convection. Third, an explanation could be that Emerald Lake may be near the edge of the "reach" of daily upslope winds. An analysis of surface wind data from Giant Forest during July 1987 indicates an average transport distance of 68.4 km (43 miles) during the 12 hours of upslope flow and 57.2 km (36 miles) during the 12 hours of downslope flow, with an average net diurnal transport of 11.2 km (7 miles) upslope.

The statistical analysis also lends support to the observations above and suggests a weaker link between the ozone concentrations at Emerald Lake and Giant Forest than between those at Giant Forest and Ash Mountain.

Recommendations

The data collected in this research project indicate that ozone concentrations at Ash Mountain and Giant Forest frequently exceed the California standard. Furthermore, mean concentrations at these two sites are higher than mean concentrations on the valley floor at Visalia. These findings support the conclusion of other researchers: the western slopes of the Sierra Nevada are impacted by elevated ozone concentrations. Because of the substantial evidence for injury to forest vegetation by ozone in Sequoia National Park (and elsewhere in the Sierra Nevada), there is a critical need for ozone monitoring in remote areas where forests are located. As indicated in this report, however, remote ozone monitoring is a difficult task. Our experience clearly shows the need for thorough laboratory evaluation of ozone monitors prior to their use for remote monitoring to determine their behavior under typical field conditions. We believe it is essential that provision be made for frequent on-site calibration, as at standard CARB monitoring stations. It is also essential that calibrations be performed against a transfer standard at the elevation where the remote monitoring is to take place. Such calibrations could be performed with a suitable reduced-pressure chamber. Research is underway on alternative ozone monitoring techniques potentially more suitable for remote use than chemiluminescent or UV-photometric monitors (Flores 1988; Cronn and Campbell 1988).

GLOSSARY OF TERMS, ABBREVIATIONS, AND SYMBOLS

Analytical Techniques

FAST	= Forward Alpha Scattering Techniques (H to F)
LIPM	= Laser Integrating Plate Method (C soot)
PIXE	= Particle Induced X-ray Emission (Na to U)
XRF	= X-Ray Fluorescence (Ca to U)
PESA	= Proton Elastic Scattering Analysis (H)

Sampler Systems

DRUM	= Davis Rotating Unit for Monitoring Sampler
SFU	= Stack Filter Unit
SPASI	= Solar Powered Aerosol Sampling Impactor
VI	= Virtual Impactor

Other

AQG	= Air Quality Group
ARB	= Air Resources Board
CARB	= California Air Resources Board
CNL	= Crocker Nuclear Laboratory
UCD	= University of California, Davis
UCSB	= University of California, Santa Barbara
UCR	= University of California, Riverside
EPA	= US Environmental Protection Agency

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